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THE

PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND
THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS, ERNEST MERRITT,
AND FREDERICK BEDELL

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THE

PHYSICAL REVIEW.

FALSE SPECTRA FROM THE ROWLAND CONCAVE GRATING.

By Theodore Lyman.

IT is proposed to show in the following paper that among the spectra formed by the Rowland concave gratings there are spectra not accounted for by the ordinary theory of the grating; that such spectra are common and at times fairly strong and of excellent definition; that these spectra are diffraction spectra, of much less dispersion than the ordinarily recognized spectra, and that the errors of ruling to which they are due are not local but general to the whole surface of the grating. Finally it is proposed to explain an experimental method by which these false lines can be sorted out from the regular and calculable overlapping spectra. These lines are especially dangerous in series spectra work, giving a somewhat systematic reproduction of strong lines and groups, which reproductions in actual vibration frequencies do not exist. There is probability and some evidence that such errors have been committed in the past, and it was in the presence of this danger that the false spectra were here discovered.

In the year 1893, Schumann showed that the ultra-violet spectrum could be extended to the neighborhood of 1,000 μ. He used a spectroscope fitted with a fluorite prism and fluorite lenses. The apparatus was so constructed that it could be enclosed in a case from which the air could be exhausted. According to his investigation, it was chiefly the absorption of the air for light of very short wave lengths that had prevented other investigators from extending the spectrum below wave length 1,800 μ. Owing to the nature of a prism spectrum, it was difficult for Schumann to determine accurately the wave lengths of the lines which he discovered. Since his paper, no attempt seems to have been made to measure these lines. It was in an effort to determine these wave lengths that the false spectra above referred to were first observed.

It seemed probable that if a concave grating could be used to obtain the ultra-violet lines, an accurate determination of their wave length would be possible. Accordingly, some two years ago, Mr. E. H. Colpitts and the writer undertook the investigation. The methods used and the results obtained were briefly as follows:

The concave diffraction grating, slit and photographic plate were all enclosed in an air-tight cast iron box. Light was admitted to the box through a fluorite window. The source of light was a powerful electric spark, obtained from a transformer run from the commercial circuit; a capacity equivalent to four large Leyden jars was placed in parallel with the spark gap; magnesium was used for terminals. Following Schumann's work, the air was exhausted from the box. The spark was placed close to the fluorite window in order that the column of air between the source and the plate should be as short as possible. Under these circumstances a photograph was obtained showing lines apparently down to wave length 924 μ, a value lower than Schumann's lowest estimated wave length. Terminals of aluminum, cadmium, cobalt, nickel and copper were tried. All showed lines below 1,800 μ; some showed lines as far down as position 950 μ.

During these experiments, the air pressure in the apparatus did not always have the same value. Some plates were taken with the pressure as high as 1 cm.; others with it as low as .2 cm. It was observed that this difference in pressure did not have any effect on the strength of the lines. Up to this time the first spectrum had been used; now it was desired to find these lines in the second spectrum. In spite of the greatest care, however, no trace of any line below 1,900 μ could be found in the second spectrum.

The absence of the lines in the second spectrum, together with their behavior under small differences of air pressure, raised the suspicion that, either the lines were not due to light of a very small wave length, or that light of very short wave length was not absorbed by the air to the extent indicated by Schumann. To test this idea the spark was first removed to a metre's distance from the fluorite window. This air column did not reduce the intensity of the new lines. Next air was admitted to the box, and still the lines were unchanged in intensity, even through a column of air now five metres long. Evidently the lines were not absorbed by air.

Lest the special brand of plate employed was particularly sensitive to the extreme ultra-violet, a number of different plates were tried. In each case a good photograph was obtained showing practically all the lines.

A piece of window glass was placed between the slit and spark and no trace of the lines could then be found. Since the light causing these lines is absorbed by glass and is not absorbed by air, it would seem to have a wave length between 3,500 μ and 2,000 μ, according to the accepted absorbing power of these two media.

It was now observed that the groups in the magnesium spectrum at 2,790 μ, 1,873 μ and 924 μ were, even to casual inspection, strikingly characteristic and identical in general appearance. Further, on measuring their dispersions, they were found to be proportional to the displacements of the groups from the slits. Therefore, these groups formed either a remarkable series reproduction or a heretofore unobserved diffraction phenomenon. Thus the issue was definitely raised whether these lines were real first spectrum lines, produced by light of wave lengths 924, 1,873 and 2,790, and arranged in a 1, 2, 3 series, or whether they were all produced by light of one wave length and owed their position to some diffraction phenomenon connected with the grating.

To distinguish between these alternatives, recourse was had to the relative refrangibility of these lines through quartz. To this end a small angle quartz prism was placed between slit and grating and a short distance from the slit. The effect of this prism was to produce virtual images of the slit whose displacements were nearly proportional to the refrangibility of the light. This device resulted in the displacement of each line in the grating spectra by an amount proportional to the refrangibility of the light producing that line.

If the lines at 1,873 μ and 924 μ were caused by light of the same wave length, they would suffer equal displacements. If they were caused by light of different wave lengths, they would be displaced by different amounts.

The experiment was tried and it was found that the groups at 2,790 μ, 1,873 μ and 924 μ all suffered about equal displacements. From 2,790 μ down to the region of 1,873 μ, the displacement of the groups increased as the wave length decreased. There was then a discontinuity in the rate of increase of the displacement before 1,873 μ and a second discontinuity between 1,873 μ and 925 μ.

The most obvious conclusion from these data is that the lines at 1,873 μ and 924μ are not due to light of wave lengths corresponding to the positions of the lines in the spectrum. They seem to be caused by light having a wave length near 2,800 μ; they seem to be reproductions of some part of the true spectrum, curious phantom lines due to some property or imperfection of the grating. An examination of the lines below 1,900 μ taken with aluminum terminals fully carried out this theory.

Before leaving this first grating, which we will call No. 1, it is important to note that although the groups in magnesium at 2,790 μ, 1,873 μ and 924 μ closely resemble each other, their wave lengths are not exactly in the 1 : 2 : 3 ratio, 2 × 924 = 1,848 which differs from 1,873 by 25 μ.

It was proved that these phantom lines were not due to any local variation in ruling by shielding all but a narrow strip of grating surface, and then moving the screen so as to expose each strip in turn. In this way a series of photographs were obtained, each from a different strip of grating surface. They all showed the phantom lines with about equal intensity.

In addition to the grating with which the investigation was begun, three others were examined. Two of these were of larger radius—21 feet, the other was similar in type to the first instrument. Of the two large gratings, one showed the phantom lines distinctly. The two strong groups formerly at 1,873 μ and 924 μ were now found at positions corresponding to 1,728 μ and 1,079 μ. The other large grating did not show the lines at all. The last small grating showed the reproduction of group 2,790 μ at positions of about

1,870 μ and 924 μ. In addition, however, there were also numerous less distinct reproductions scattered between these two positions.

We may now sum up the facts arrived at in these few pages. Of four concave diffraction gratings examined in this investigation, three showed the phenomenon of phantom lines. These lines vary in position with the grating by which they are produced, but the variation cannot be connected either with the variation of radius of curvature of the grating or with the number of lines to the inch. The most prominent of these phantom lines closely resemble some group in the true spectrum. This repetition of a true group occurs most strongly twice. The width of these phantom repetitions is proportional to their apparent wave length. The wave lengths of the true group and its phantom repetitions bear no simple relation to one another. The photographs obtained with gratings 1 and 4 show a very large number of faint repetitions of a group or set of groups. These repetitions form a sort of background to the main spectrum between 1,800 μ and 900 μ.

A more detailed account of the apparatus and of the numerical results of the investigation will now be given. The consideration of the causes which produce these phantom lines is left for the end of the paper.

The first grating investigated was one of 180 cm. radius. The plate was prepared by Brashear and ruled by Rowland's engine in the year 1897; it had 14,438 lines to the inch. To economize space a mounting somewhat different from that of Rowland was used. The grating and slit were fixed in position at a distance apart equal to the radius of curvature of the grating. The plate-holder was carried by an arm pivoted at a point on the line connecting slit and grating and midway between the two. The length of the arm was, of course, half the radius of the grating. The plane of the grating was so adjusted that the principal image fell about 2 cm. to the right of the slit. This was done to avoid reflection from the polished jaws of the slit. The plate-holder was constructed to take a plate 5 inches long and 1 inch broad. The form of the box in which the apparatus

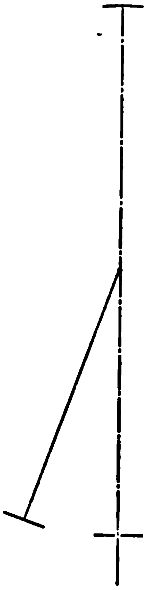

Fig. 1.

was enclosed is not material to this investigation. The spark which served as a source of light was placed within 3 mm. of the fluorite window. In the first experiments the width of the slit was about .1 mm. and the time of exposure was about 1 hour. Later, however, good photographs were obtained with exposures of from 12 to 15 minutes. In making tests for the absorption of the air a quartz lens was placed between the source and the slit.

In developing photographs of this type, great contrast is the chief object. The kind of developer used thus becomes important. After several trials, an Ortol-Soda developer was found to give the best results.

The apparent wave lengths of the different lines which come under consideration were determined by comparison with the normal sun spectrum. A dividing engine with a ½ mm. screw was used. This screw, when used to measure lines on a 6-foot grating possesses for a run of 20 cm. an accuracy better than one one-hundredth of an Ångström unit. The plate was observed by means of a stationary microscope fitted with a 4-inch objective and micrometer eye piece. The value of one centimeter of plate length in terms of Ångström units was determined by measurements taken between two given sun lines, located by Rowland's map. In order to get a photograph of the sun spectrum and the magnesium spectrum on the same plate, a shutter was placed before the slit and so adjusted that the upper or lower half could be exposed at pleasure. By this means two narrow spectra were obtained, one above the other. The method is preferable, when working with the first spectrum, to the usual mode of protecting the plate itself by a swinging screen.

When it became necessary to test the nature of the light producing the lines at 1,873 μ and 924 μ in the magnesium spectrum, the following arrangement was adopted. The quartz prism of an angle of 5 degrees was placed some 30 cm. distant from the slit, but not on the straight line joining slit and grating. Thus when the source was in position *A*, the light did not fall upon the prism; but when it was in position *B*, the light passed through the prism. In the first case, the upper half of the slit was closed by the shutter; in the second, the lower half was closed. The result was, of course, to produce two spectra, one above the other; the one due to light

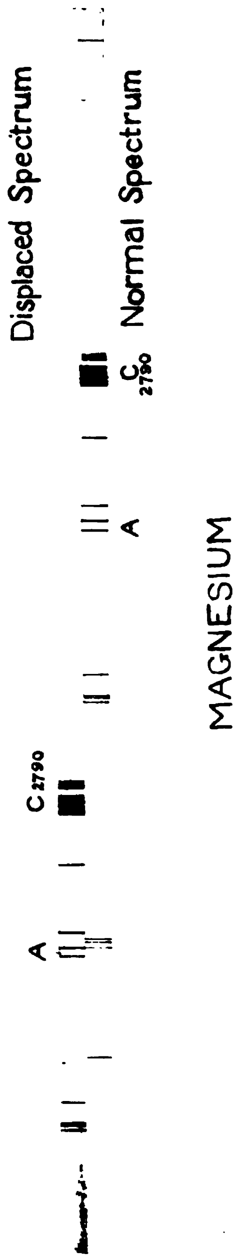

Fig. 3.

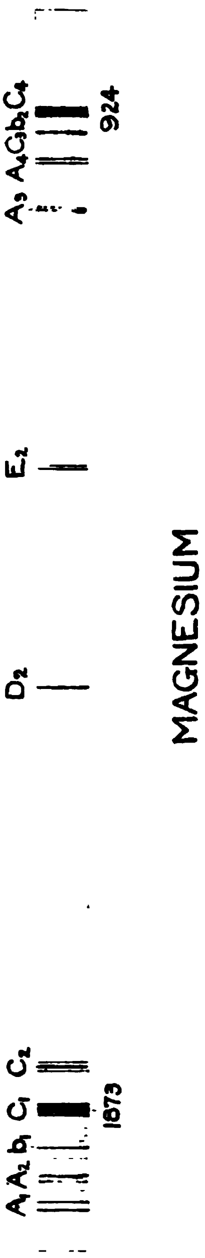

Fig. 4.

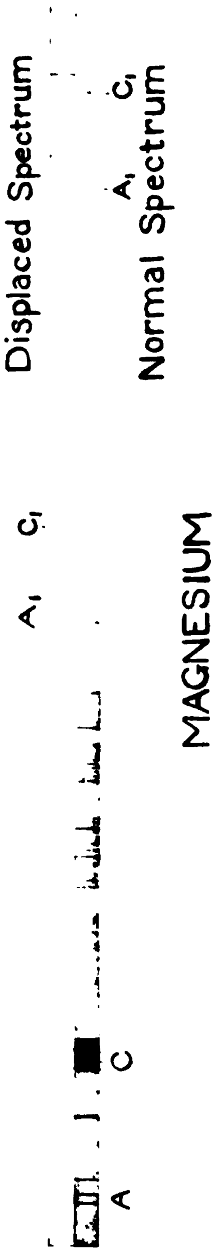

Fig. 5.

LYMAN: FALSE SPECTRA FROM THE ROWLAND CONCAVE GRATING.

which had passed through the prism was thus shifted toward the red. The general appearance may be seen from Fig. 3, Plate 1.

It now becomes necessary to consider more in detail the behavior of the light of these ultra-violet spectra when passed through the quartz prism. The results for magnesium may be seen from the following table. The lettering of the groups on the plans of the spectra is, of course, arbitrary. The chief or real groups are marked with an unsubscripted letter. The reproductions are marked with letters bearing a subscript. The plates are from drawings made from the original photographs. Beginning with magnesium, Fig. 4, six principal groups of lines are to be noted, they extend from the pair of lines marked A_1, wave length 1,966 μ to the strong group C_4, wave length 924 μ. Besides these strong lines, there are six fainter groups distinctly visible, A_2, B_1, C_2, A_3, B_2 and C_3. A_2 resembles group A_1, C_2 group C_1; C_3 resembles group C_4, A_3 group A_4. It is to be noted that while A_2 and C_2 lie on the right or ultra-violet side of A_1 and C_1, C_3 and A_3 lie on the left or red side of C_4 and A_4. In addition to the simple groups of lines already mentioned, the whole spectrum, from one end to the other between A_1 and C_4 is filled with a number of fine, faint lines. These lines are not regularly arranged so as to produce fluting, but rather present the appearance of a reproduction of groups of lines.

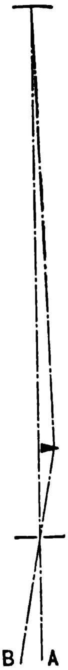

Fig. 2.

If we examine the displacements produced in these groups when the light is allowed to pass through the quartz prism before falling upon the grating, the following facts become evident. A steady increase in displacement is observed in the successive lines going from the strong group at 2,790 μ (C) towards the ultra-violet until we get in the neighborhood of group A_1. At this point the amount of displacement suddenly returns to about the value it had at 2,790 μ. Between groups A_1 and D_2 the displacement suffers a second discontinuity. Thus A_1 gives 42.1 mm., D_2 39.8 mm. The displacement of C_4 is almost exactly that of C_1 and very nearly that of group C, 2,790 μ. The figures are 42.25 mm., 42.25 mm., 42.21 mm. As stated before the most obvious conclusion from these data is that the lines A_1 to C_4 are not due to light of wave lengths corresponding to the positions of the lines in the spectrum. They seem to be reproductions of some part of the true spectrum.

On the aluminum plate, there are present six strong lines B_1, C_1, D_2, E_2, B_3, C_3 with wave lengths from 2075 μ to 933 μ. There are faint reproductions of these groups similar in arrangement to those observed with magnesium. There is a background of fine indistinct lines. On allowing the groups to be displaced by the prism, we find group D_2 less displaced than group C_1, and group B_1 less displaced than a real group called *I*.

Magnesium.

Group.	Apparent wave length.	Displacement.
C.	2790 μ	42.2 mm.
I.	2713.	43.4
II.	2682.	43.9
A_1.	1966.	42.1
A_2.	1924.	
b_1.	1914.	
C_1.	1873.	42.2
C_2.	1834	42.3
D_2.	1475	39.8
E_2.	1266	40.2
A_4.	969	41.9
C_3.	964	
b_2.	944	
C_4.	924.	42.2

Aluminum.

Group.	Apparent wave length.	Displacement.
I.	2376 μ	38.8 mm.
B_1.	2075	36.1
C_1.	1890	36.7
D_2.	1300	34.9
E_2.	1184	35.3
B_3.	1023	36.0
C_3.	933	36.6

We may now consider the false nature of the lines as established. It remains to investigate the causes which produce this diffraction phenomenon.

It is perfectly evident that the phantoms are not due to a local variation in the rate of ruling, such as produce ghosts; for we have seen that the fault is not local in the grating surface. Moreover, we know that a ghost always occurs close to the line of which it is a reproduction.

The phantoms are not due to a false source of light since the dispersion of the various reproductions is not the same as that of the real group. We may discard the hypothesis that the mounting of the grating or the position of the source of light has any effect. The lines occur with various forms of mounting and with various positions of lens and source, as will be seen later. We have to deal with a diffraction phenomenon, with an inherent property of the diffraction grating itself.

It seems probable that in developing the theory of the grating some assumptions have been made which are not according to fact. It is in the error of such assumptions that we must seek the solution of our problem.

It is generally assumed in treating the grating that the lines of the ruling are of equal width and are separated by equal spaces. In the very nature of things, it is evident that this cannot be the case in view of the very minute distances involved and the almost inconceivable rigidity of the ruling engine which would be necessary. These variations, slight in absolute amount, may be a considerable fraction of the distance from line to line. It is clear, moreover, on experimental as well as on the theoretical ground that these variations are not local but extend over the whole surface of the grating.

It appears, then, that the departure from equal spacing assumed in the theory of the concave grating, is not the random departure which is next in theoretical simplicity, but a more or less systematic departure which has emphasized disproportionately certain of the subordinate maxima called for in the conventional theory. If the position of the false maxima occurred in the ratio 1 : 2 : 3, or in any other simple ratio, the phenomena would invite an analytic discussion. As an experimental fact, however, our lines are not harmoniously placed with respect to the slit, nor are they arranged according to any discoverable system. Moreover, they are different in character and position when obtained by different gratings ruled by the same engine. It seems most likely that the phantom lines are due to a number of superposed first spectra of varying dispersions;

and that these false spectra owe their existence in some manner to the variation in width and separation of the grating lines. Under these conditions, an analytic discussion seems less profitable than the presentation of the experimental data.

In order to substantiate the statements just made, it becomes the next object of the investigation to observe carefully the relative positions of the phantom lines, not only in one, but in several different gratings.

We must carefully observe, in looking over the tables already given, that although several groups bear a strong resemblance to each other, and though the apparent wave length of these groups are nearly in one, two, three ratio, this ratio is never exact.

In aluminum, the line C_3 seems to resemble the line C_1, but $2 \times 933 = 1{,}866$ not 1,890. The group B_3 resembles B_1, but $2B_3 = 2{,}046$, not 2,075. There certainly is no exact 1, 2, 3 relation, although lines corresponding roughly to $3C_3$ and $3B_3$ in wave length may be found for aluminum. The difference between $2{,}046\,\mu$ and $2{,}075\,\mu = 29$ Ångström units cannot possibly be due to the error of observation. It is perfectly safe to say that the measurements of wave lengths in the table are correct to 1 Ångström unit.

Before examining another grating, there are one or two more points which need attention. A concave grating produces two spectra of the first order, which in this form of mounting lie on each side of the slit. The spectrum on the left had been investigated, it was now necessary to observe the spectrum on the right of the slit. The grating was therefore turned upside down, by which process the spectrum formerly on the right of the slit now fell upon the left. Photographs taken showed the lines, A_1, C_1, A_4, C_4, etc., in magnesium as clearly as before. The grating was next turned about a vertical axis until the direct image of the slit fell upon the plate. No lines below group C_4 were revealed by this process, nor was the position of the lines greatly changed. It must be noted, however, that the turning of the grating will somewhat distort the spectra and change the value of μ to cm.

The second grating to be investigated was of 21 ft. radius, 14,438 lines to the inch. It was arranged on Rowland's mounting. The intensity of the spectra given by this grating was very inferior to that obtained with the 6 ft. instrument. The first spectrum was selected to work with, the magnesium spark was used as a source. It was found necessary to give an exposure of an hour and to use a slit .2 mm. in width. A good deal of care was taken to have the exposure of the proper length; if too short, the lines themselves would not appear; if too long, the lines would be obscured by fog. With this 21 ft. grating, a very little fog would quite shield any very faint line. After some trouble, the characteristic reproductions of group 2,790 μ were found. They now occurred, however, at positions corresponding to wave lengths of 1,728 μ, 1,079 μ. The widths of the groups were 4.8 mm., 2.8 mm., 1.8 mm. Thus, though these phantom lines have different apparent wave lengths when measured on different gratings, their dispersion seemed proportional to the wave length. It must be noted that with grating No. 2 only the lines called A_1, C_1, and A_4, C_4 are visible; the other fainter lines, as well as the fluted effect in the background being totally absent. This is well accounted for by the feebleness of the spectrum obtained from grating No. 2. The apparent wave length of these groups was obtained by the same method as that previously employed. Owing to the great distance between the head group (2,790 μ) C and its reproductions, a cathetometer was used. The results are correct, however, to better than 2 Ångström units. The widths of the groups were measured on the dividing engine and are correct to within .03 mm. The value of 1 cm. of plate length was obtained from measurements between two sun lines.

It would be interesting to take groups C_4 and C_1 on one very long plate, and group C_4 and the image of the slit on another. By this method the wave lengths of C_4 and C_1 could be very accurately determined. As it is, however, I feel certain that groups 2,790 μ C_1 and C_4 as obtained with grating No. 2 are not in 1 : 2 : 3 ratio.

The next grating investigated was one of 21,000 lines to the inch and 21 ft. radius. Here the illumination was even more feeble than with grating No. 2. Great trouble was experienced from fog. The lines in magnesium, C_1 and C_4 could not be found. The last grating examined was similar to No. 1. It has a radius of 183 cm., 14,438 lines to the inch; it was prepared by Brashear; it was ruled by Rowland's engine at Johns Hopkins in the year 1894. The mounting was the same as that of grating No. 1.

The character of the photographs obtained with grating No. 4 was quite different from those obtained with grating No. 1. Lines A_1, C_1 and A_4, C_4 were present and with about the same apparent wave length as before. They were, however, very much less distinct than when obtained with grating No. 1. The fluting effect was not very sharp; but, on the other hand, the space between positions 1878 μ and 924 μ was filled with reproduction of groups A_1 and C_1, of such clearness as to be quite unmistakable. The wave lengths of some of these phantom lines was determined in the same manner as before. Groups corresponding in appearance to the family marked A_1 A_2 A_3, etc, were found at 1,970 μ 1,020 μ and 993 μ and 970 μ. The group called C_1, C_2, etc., were found at 1,878 μ and 924 μ very clearly, and at more than eight other positions in a less distinct form between 1,878 μ and 924 μ. In fact, the spectrum in this region is so filled with groups of the A, C type that the lines of one family overlap lines of the other in many cases.

Such, then, are the experimental data connected with this phenomenon. Before coming to a statement of conclusions, however, the following facts are of interest.

Some of the reproductions belonging to the set of lines A_2 and E_2 in aluminum occur under the real spectrum and may be observed if proper care is used.

Gratings of large radius do not show the false lines with as much clearness as gratings of small radius. So feeble indeed are the false lines obtained with the 21 ft. grating that it is improbable that they would be noticeable in ordinary spectrum work. With a six foot grating, however, the false lines are so strong that they might easily cause errors in series spectrum investigations. We have seen, moreover, that the false lines from grating No. 1 are much stronger than those from grating No. 4, and we have reason to suspect that gratings exist which produce false lines even stronger in character than those obtained with grating No. 1. Gratings 1 and 4 differ little in radius and have exactly the same number of lines to the inch, yet their false spectra are entirely different in character.

We cannot apparently predict the nature of the false spectra of one grating from the false spectra produced by another of the same ruling and radius.

The conclusions arrived at in this paper may be stated as follows:

1. The first spectrum produced from the Rowland concave grating is not pure, but is complicated not only by underlying spectra of higher order, but by the presence of a number of spectra of lower dispersion than the chief spectrum.

2. The number and dispersion of these false spectra obey no simple law.

3. The number, dispersion and clearness of these spectra differ with different gratings.

4. The lines due to the false spectra are most clearly visible in the extreme ultra-violet, owing to the absence of strong real lines, and are so pronounced as to screen the feeble real line that may occur in this region.

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A MODIFICATION OF THE USUAL METHOD OF DETERMINING TRANSFERENCE NUMBERS AND AN INVESTIGATION OF THE INFLUENCE OF THE CONCENTRATION ON THEIR VALUES IN THE CASE OF SOME TRI-IONIC SALTS.

By Arthur A. Noyes.

1. Purpose of the Investigation.

As has been frequently pointed out, the dissociation of tri-ionic salts, such as potassium sulphate and barium nitrate, like that of most dibasic acids, might well be expected to take place in the two stages expressed by the following equations:

$$K_2SO_4 \rightleftarrows K^{\cdot} + KSO_4' \quad \text{and} \quad KSO_4' \rightleftarrows K^{\cdot} + SO_4'',$$
$$Ba(NO_3)_2 \rightleftarrows BaNO_3^{\cdot} + NO_3' \quad \text{and} \quad BaNO_3^{\cdot} \rightleftarrows Ba^{\cdot\cdot} + NO_3'.$$

Up to the present time, however, no conclusive experimental evidence of the existence of such intermediate complex ions as KSO_4' and $BaNO_3^{\cdot}$ has been presented. The freezing-point lowering and electrical conductivity of such salts prove, to be sure, that, even in moderately concentrated solutions, the intermediate ions, if they exist at all, are present only in relatively small amounts. Nevertheless, the question is still unanswered, whether the portion of the salt that is not completely dissociated consists wholly of undissociated molecules (K_2SO_4 and $Ba(NO_3)_2$) or mainly of the partially dissociated ones (KSO_4' and $BaNO_3^{\cdot}$). The answer to this question cannot be reached by the method used in the case of dibasic acids, since it is only for hydrogen and hydroxyl ions that we possess specific quantitative methods of determination. The property adapted to throw the most light on the matter would seem to be the change of the transference numbers of such salts with the concentration; for if KSO_4' or $BaNO_3^{\cdot}$ ions exist in moderately concentrated solution and if these ions are dissociated in diluter solutions, as they must be, into K˙ and SO_4'' or Ba˙˙ and NO_3 ions, it is evident that the proportion of potassium or barium transferred in the differently concentrated solutions will be markedly different.

This investigation was therefore undertaken in order to determine the effect of dilution on the transference numbers of some tri-ionic salts. Since the results, to be of much value in connection with the theoretical question just referred to, must have a high degree of accuracy, my first efforts were, however, devoted to perfecting the usual method of determining transference numbers, and these have led to a modification of it, which it is one of the main purposes of this article to describe.

2. Results of Previous Investigators.

Before describing my own experiments, the results of previous investigators bearing directly on the subject may be mentioned.

In the first place, it may be recalled that various investigators have proved that the transference numbers of *di*-ionic salts do not vary with the concentration, provided the latter does not exceed a moderate value, for example, 0.5 mol per liter. Thus, this has been shown by Hittorf in the case of potassium chloride, bromide, iodide, chlorate, nitrate, cyanide, and acetate, ammonium chloride, sodium chloride, nitrate, and acetate, and silver nitrate. This constancy of the transference numbers has been confirmed by other investigators[1] in the case of many of these salts, and has been found by Loeb and Nernst[2] to apply also to silver acetate and silver ethylsulphate. The only exceptions thus far discovered are in the cases of lithium iodide and chloride, which have been found by Kuschel[3] and Bein[4] to behave like the halides of the alkaline-earth metals (see below). Aside from these exceptions, which are probably to be explained by assuming the formation of intermediate complex ions, the statement made above in regard to the non-variations of transference values with the dilution holds true.

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[1] For the original literature on transference determinations, see Bein, Ztschr. physik. Chem., 27, 1. For a summary of all existing values for concentrations up to 0.1 normal, see Kohlrausch, Wied. Ann., 66, 816.

[2] Ztschr. physik. Chem., 2, 948.

[3] Wied. Ann., 13, 289.

[4] Ztschr. physik. Chem., 27, 50.

Hitherto only very few tri-ionic salts have been satisfactorily investigated in this direction. Aside from the earlier experiments of Hittorf, Weiske, Kuschel, and others, which are not sufficiently accurate to throw any light on the present question,[1] and aside from the more recent experiments on the halogen compounds of cadmium and zinc, which exhibit unusually complicated relations, the only determinations available for our purpose are those of Bein[2] on barium, strontium, and calcium chlorides, and of Hopfgartner[3] on barium chloride. It is desirable that even these determinations should be confirmed, since the results obtained are somewhat remarkable in their character. It was found, namely, that the transference number of the cathion increases with increasing dilution, which is just the opposite of the effect which would arise from the presence of $BaCl^{\cdot}$ or $CaCl^{\cdot}$ ions in the more concentrated solution. Barium chloride was, therefore, included among the salts which I have investigated. The significance of the behavior which it exhibits will be further considered below.

3. Description of the Method.

As is well known, the principal difficulty met with in determining the transference numbers of salts for which electrodes of the same metal can not be used arises from the fact that free alkali and acid are generated at the cathode and anode respectively and that the hydroxyl and hydrogen ions thus produced, on account of their high rates of migration, rapidly pass into the middle portions of the solution, thus changing its composition and its transference relations.[4] This change in composition can be greatly retarded on the anode side by the use of a cadmium electrode, since the cadmium ions that pass into solution have a rate of migration very much smaller than that of hydrogen ions. This kind of anode has in fact been generally employed.[5] There has been, however, no equally satisfactory method described for preventing the dispersion of the hydroxyl ions produced at the cathode,[1] and Hittorf, Bein, and others in their investigations have simply taken care to stop the electrolysis before the alkali had reached the middle portions.

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[1] Compare Bein, Ztschr. physik. Chem., 28, 439–452, in regard to the errors of the early determinations; also Kohlrausch, Wied. Ann., 66, 818, in regard to the disagreement of the results of them.

[2] Ztschr. physik. Chem., 27, 50, 51.

[3] Ztschr. physik. Chem., 25, 137.

[4] See Bein, Ztschr. physik. Chem., 27, 3–18, for a full discussion of this matter.

[5] Compare Bein, Ztschr. physik. Chem., 27, 21, in regard to the source of error arising from the deposition of small quantities of basic salt on the anode.

This procedure is, however, open to the objection that the absolute amount of substance transferred is necessarily small, and since this small amount is obtained as a difference of two much larger experimentally determined quantities, the percentage errors in the final results are necessarily large. Thus in Bein's experiments on metallic chlorides, which are probably the most accurate with polarizable electrodes thus far published, the amount of chlorine transferred was in almost all cases between 9 and 40 milligrams, and this value was obtained by subtracting two quantities usually 4–10 times as great. It is true, to be sure, owing to the great accuracy of the volumetric determination of chlorine, that the corresponding transference values exhibit an average deviation from the mean of only 0.6–0.7 per cent.[2] This degree of accuracy could probably not be reached in the case of most other ions, and even it leaves very much to be desired.

It occurred to me now that the difficulty just considered, arising from the dispersion of the hydrogen and hydroxyl ions into the solution, might be entirely obviated by the simple device of gradually adding during the electrolysis to the solutions around the cathode and anode, sufficient amounts of the acid and base, respectively, of which the salt is composed, to keep those solutions neutral (or, preferably in practice, slightly acid and alkaline, respectively). If, furthermore, the acid and base added are dissolved in suitable quantities of water, it is evident that not only the formation of new substances around the electrode may be prevented, but also that the changes of concentration of the original salt due to transference may be compensated, so that the whole solution will remain unchanged in composition, and the electrolysis can be continued indefinitely. Thus, if the transference number (which is approximately 0.5) of a

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[1] Both Lenz and Hopfgartner with this purpose in view, covered the cathode, which consisted of mercury, with concentrated zinc chloride solution, but this prevented an accurate analysis of the solution around the cathode.

[2] This estimate is based on a consideration of Bein's results with the chlorides of the alkali and alkaline-earth metals at ordinary temperatures (pp. 49–51 of his article).

0.2 normal potassium sulphate solution were to be determined, one would add gradually at the cathode 0.4 normal sulphuric acid in such (measured) amounts, determined with the help of an indicator or calculated from the electricity passing through, as will keep the solution slightly acid; and would add at the anode an equal amount of 0.4 normal potassium hydroxide. If, however, the transference number of the positive ion were 2/3 and the salt 0.2 normal as before, the acid solution used would have to be 0.3 and the base solution 0.6 normal, and the volume of the former added would have to be twice that of the latter, in order to keep the concentration constant. In practice, however, it is desirable that the added solutions should be somewhat stronger (or weaker) than the theory requires, in order to prevent the solution around the electrodes from rising (or sinking) into the middle portions.

Three salts, potassium sulphate, barium chloride, and barium nitrate, were investigated in the order in which they are here named, each one at two concentrations, 0.1 and 0.02 molar.[1] The samples used were prepared by recrystallizing the commercial chemically pure salts two or three times from water. In the case of the potassium sulphate, the analyses of the solutions, both before and after the electrolysis, were made by evaporating them, after exactly neutralizing, if necessary, with sulphuric acid, to dryness on a water bath in platinum dishes, and igniting the residue, at first very gently and then intensely. Great difficulty was experienced by reason of decrepitation on first heating; but this source of error was entirely removed by tying ash-free filter-paper closely over the top of the dish, heating carefully only the bottom of the dish so as to avoid igniting the paper, and afterwards incinerating the latter. In the case of the two barium salts, the analyses were made by adding a slight excess of sulphuric acid to the solution, evaporating to dryness as before, and igniting the residue to a constant weight at a moderate red heat. During the evaporation, the dishes were covered with filter-paper (which was afterward incinerated), in order to avoid a loss of the precipitate by spattering, occasioned by the escape of small bubbles of air from the solution. This subtle source of error caused, before it was discovered, the loss of several transference determinations. The barium hydroxide solution added at the anode was, in the case of the barium nitrate experiments, analyzed in just the same manner.

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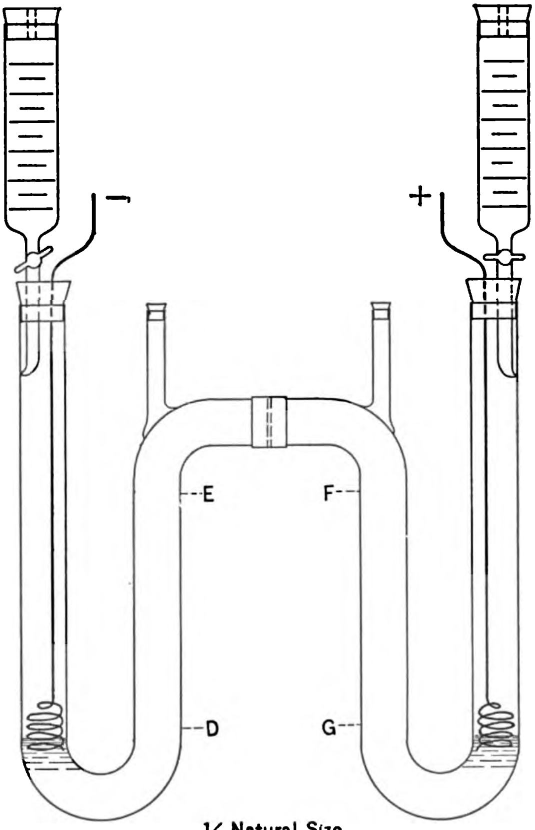
[1] I use this term (previously suggested by Ostwald) to designate the concentration of solutions containing one mol (one molecular weight in grams) in one liter of solution. The general introduction of some such term seems highly desirable, first in order to avoid a very frequently occurring circumlocution, and second, in order to avoid the serious confusion which is beginning to arise through the double use, by some writers, of the term *normal*, namely its use in this sense, as well as in its appropriate sense of one equivalent per liter.

The method employed in carrying out the transference experiments with barium nitrate was somewhat different in its details from that used in the case of the other two salts. I will first fully describe the former method, for it has, I believe, some advantages over the latter; and will then briefly mention the respects in which the two methods differ.

At the beginning of each experiment, the apparatus, shown in the accompanying sketch, consisting essentially of two large glass U tubes, 3.5 cms. in diameter, joined by a piece of soft rubber tubing, was charged with such an amount of barium nitrate solution that the whole middle part of the U tubes and their side-arms up to a point about 2 cms. above the top of the bend were filled with it. Rubber stoppers were inserted in the small upright arms on the middle of the tube, so as to keep the solution in place. To the portions in the bends were added a few drops (a known weight) of phenolphthalein solution, in order to assist in regulating the addition of alkali and acid. The indicator is rapidly decolorized in the immediate neighborhood of the anode, but is nevertheless useful, since it retains its color in the bend beneath. Cork stoppers with one large and one small hole were inserted in the top of each side arm. Through the small holes passed heavy platinum wires bent at the bottom into the form of a spiral. These were made to dip only a few millimeters into the solution, and were gradually raised during the electrolysis so as to be always near the top of the liquid. The distance between the electrodes was 80 to 100 cm. Through the larger holes in the stoppers were inserted the stems of cylindrical drop-funnels, like those shown in the drawing. These were graduated with divisions corresponding to each 5 cc. The stems were bent slightly at their ends and drawn to a point, so as to cause them to remain full of liquid and to deliver against the sides of the U tubes. These two drop-funnels were filled at the start with approximately 0.5 normal nitric acid[1] and barium hydroxide for the experiments with the more concentrated solution, and with 0.1 normal acid and base for those with the more dilute. These funnels, which were closed above with one-hole rubber stoppers, were weighed to the nearest centigram before and after the electrolysis, the stems being capped with small test-tubes during the



1/6 Natural Size.

Fig. 1.

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[1] The acid solution used in the first experiments was prepared by diluting the concentrated acid with the pure distilled hydrogen peroxide solution, in order to entirely prevent reduction of the nitrate to nitrite and ammonia; but this precaution was later dispensed with, as it was found to make no difference in the results.

weighing. The base solution was protected from the air during the electrolysis by a soda-lime tube inserted in the rubber stopper.

At least twenty minutes before the electrolysis was started, the U tubes were immersed in a large thermostat at 25°, to such a depth that the middle horizontal part of the apparatus was entirely covered. After the temperature differences had become equalized, 2.5 cc. of the nitric acid solution were added at the cathode and 10 to 15 cc. of the barium hydroxide solution at the anode. This excess of the latter was added at the start, in order to make the anode solution distinctly heavier than the middle portion above, and to introduce into the bend enough free base to neutralize any acid which might escape neutralization in the immediate neighborhood of the electrode. The electrodes were then connected through a switch, two 32-candle-power lamps, a Weston milliammeter, and a silver voltameter, all in series, with the terminals of the city-circuit of 110 volts potential; and the current was turned on. The silver voltameter consisted of a platinum dish (serving as cathode) which contained a 15 per cent. silver nitrate solution, just beneath the surface of which was placed a horizontal silver plate (to serve as anode) which was wrapped with filter paper and supported by a silver rod riveted through it. The milliammeter served merely to indicate the strength of the current, and was not used for a quantitative determination of it.

As the electrolysis proceeded, at intervals of 10–12 minutes, each time as soon as the pink color appeared at the cathode, 2.5 cc. of the nitric acid and an equal volume of the barium hydroxide solution were added. The electrolysis was continued for about three hours. At the end of this time the electrodes and drop-funnels were removed, perforated rubber stoppers were inserted in the side arms, their holes were closed by pushing in pieces of glass rod, and the stoppers in the small middle arms were taken out. Through these arms three middle portions (lying between the points *E* and *F*, *D* and *E*, and *F* and *G* in the figure) were slowly removed by means of a pipette connected with a suction pump, the tip of the pipette being gradually lowered so as to be always just beneath the surface of the liquid; the portions were then transferred to small flasks. The apparatus was next removed from the thermostat and separated at the rubber band; the U tubes were wiped off outside with a dry cloth, the liquid on the inside adhering to the upper part of the middle arms being also removed; and the tubes were weighed separately on a large balance, after adding to the anode portion a weighed amount of dilute nitric acid sufficient to make the solution acid, thus avoiding later the absorption of carbon dioxide from the air. The contents of the U tubes were now transferred as completely as possible to small flasks, the liquid being once poured back to secure thorough mixing. The U tubes were then washed out, dried, and weighed. The flasks were all weighed, their contents poured out into the platinum dishes, and the nearly empty flasks again weighed. The weights of barium sulphate obtained from the cathode and anode portions were corrected for the small known weights of solution remaining in the U tubes.

In the case of the potassium sulphate and barium chloride experiments, only the cathode and middle portions were analyzed. The method of conducting the electrolysis was also somewhat different in these cases. The side-arms of the U tubes were at the beginning filled with solution for two-thirds of their length (instead of up to a point only a little above the bends) and the concentrations of the acid and base solutions added were made ten per cent. less (instead of greater) than would be required to maintain a constant concentration, in order to prevent the portions around the electrodes from sinking into the unchanged solution beneath. These solutions were added from burrettes with tips turned upward and delivering a little below the bottom of the electrodes, which reached as before just beneath the surface of the liquid. The weight of the sulphuric or hydrochloric acid solution added was calculated from the measured number of cubic centimeters with the help of the known specific gravity of the solution; this volume measurement is unobjectionable in the case of the acid solution added, since no non-volatile matter is introduced, and the greatest accuracy is therefore not required, but direct weighing of the base solution is far preferable in case the anode portion is to be analyzed. Both methods of charging the U tubes and of regulating the concentration at the electrodes give satisfactory results; in that last described, the middle portion is of greater length, and the electrolysis could perhaps be longer continued, if it were desired to do so. The method used in the case of the barium nitrate is preferable, however, when the base solution to be added, like that of barium hydroxide, is heavy; for, if the other method is used, it is difficult to prevent the added portions from sinking down before they become mixed with the liquid already surrounding the electrode. The electrolyses of the potassium sulphate and barium chloride solutions were continued from four to eight hours.

4. RESULTS OF THE TRANSFERENCE DETERMINATIONS.

The experimental data and the calculated transference numbers are given in the tables below. All the values given (except, of course, the current, time, and transference numbers) are weights in grams. Those in the columns relating to the salt-content are the quantities of the substances actually weighed, namely of the potassium sulphate and barium sulphate. In the second column, the portion of the solution surrounding the cathode is designated by K, the adjoining middle portion by M_I, the next one by M_{II}, that adjoining the anode portion by M_{III}, and the anode portion itself by A.

The temperature was in all cases 25°.

The original solutions submitted to electrolysis, the concentrations of which are only approximately stated in the headings, were found to contain the following amounts of salt in 1000 grams of *solution:* in experiments, nos. 1 and 2, 17.247 gms.; in no. 3, 17.205 gms.; and in nos. 4, 5, and 6, 3.4927 gms. K_2SO_4: in nos. 7, 8, 9, and 10, 22.906 gms.; in nos. 11, 12, and 13, 4.6448 gms.; in nos. 14, 15, and 16, 21.083 gms.; in no. 17, 21.099 gms.; in nos. 18 and 19, 4.6666 gms., and in no. 20, 4.6560 gms. $BaSO_4$. The barium hydroxide solution added in experiments 14, 15, 16, and 17 gave 56.443 gms. $BaSO_4$, and that used in experiments 18, 19, and 20, gave 11.700 gms. $BaSO_4$ for 1000 gms. of solution.

The values of the transference numbers, which are given in the last columns of the tables, are those of the positive ions multiplied by 100. The way in which these were calculated may be illustrated with the help of the data obtained in the first experiment with potassium sulphate (see the table below). The cathode portion submitted to analysis weighed 493.12 grams, and was found to contain 8.4394 grams K_2SO_4. To determine what it contained before the electrolysis, we must evidently subtract from the final weight of the portion, the weight of all matter which was introduced in the process of carrying out the electrolysis, and multiply the remainder by the original salt-content, which was 0.017247 gm. per gram of solution. The weight of dilute sulphuric acid and phenolphthalein added, which was 60.78 grams in this experiment, must therefore be first subtracted. Secondly, a correction must be made for the fact that the weight of the cathode portion is, by the electrolysis itself, increased by the weight of the potassium ions which have migrated into it, and decreased by the weight of sulphate ions which have migrated out of it[1] and by the weight of the hydrogen gas which escaped at the electrode. Since the average value of the transference number is found to be 0.493, the total increase of weight from these three causes would evidently be: $(39.1 \times 0.493) - (48.0 \times 0.507) - 1.0 = -6.0$ gms., for every 108 gms. of silver deposited in the voltameter, or -0.14 gm. in this experiment. The increase in the amount of the salt in the cathode portion is therefore $8.4394 - (493.12 - 60.78 + 0.14) 0.017247 = 0.9803$ gms. Adding to this the change ($+0.0013$) in the adjoining portion and dividing by the equivalent weight of potassium sulphate (87.18), and by the number of equivalents of silver precipitated in the voltameter, the transference number is found to be 0.4941. The cases where the adjoining portion suffered a change in concentration greater than the analytical error, and where consequently this change was combined with that of the cathode or anode portion are indicated in the table by a brace following the two quantities. The calculation of the transference number from the change in concentration at the anode was, in the case of the barium nitrate experiments, made in an entirely analogous manner, except that from the weight of barium sulphate obtained from the anode portion after the electrolysis, there was of course subtracted the amount coming from the barium hydroxide solution added. For the sake of greater clearness, the total weight of salt obtained from the anode portion is, in the table, resolved into the two corresponding components.

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[1] It is evidently assumed hereby, as is always done in transference calculations, that the ions are not hydrated. It may not be without value to call attention to the fact that the commonly observed change of the calculated transference numbers with the concentration may be due, wholly or in part, in the case of concentrated solutions, to hydration of the ions, and to the failure to take this into account in the calculation.

Potassium Sulphate, 0.1 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
1	K	493.12	8.4394	60.78	7.4591	+0.9803	2.4594	49.41
	$\mathrm{M_{I}}$	137.47	2.3723		2.3710	+0.0013	0.11 amp.	
	$\mathrm{M_{II}}$	204.82	3.5365		3.5326	+0.0039	310 min.	
2	K	456.48	7.7762	91.21	6.3033	+1.4729	3.6760	49.33
	$\mathrm{M_{I}}$	175.15	3.0126		3.0209	−0.0083	0.134 amp.	
	$\mathrm{M_{II}}$	86.96	1.4993		1.4998	−0.0005	415 min.	
3	K	434.79	7.4142	48.70	6.6446	+0.7696	1.9370	49.19
	$\mathrm{M_{I}}$	119.85	2.0615		2.0620	−0.0005	0.063 amp.	
	$\mathrm{M_{II}}$	133.38	2.2941		2.2948	−0.0007	460 min.	

Potassium Sulphate, 0.02 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
4	K	491.47	1.6964	56.73	1.5185	+0.1779	0.4451	49.68
	$\mathrm{M_{I}}$	103.75	0.3631		0.3624	+0.0007	0.028 amp.	
	$\mathrm{M_{II}}$	102.99	0.3599		0.3597	+0.0002	240 min.	
5	K	463.31	1.5869	84.31	1.3238	+0.2631	0.6524	49.59
	$\mathrm{M_{I}}$	176.04	0.6131		0.6149	−0.0018	0.040 amp.	
	$\mathrm{M_{II}}$	94.08	0.3289		0.3286	+0.0003	245 min.	
6	K	469.56	1.6246	57.40	1.4397	+0.1849	0.4617	49.58
	$\mathrm{M_{I}}$	103.17	0.3604		0.3603	+0.0001	0.018 amp.	
	$\mathrm{M_{II}}$	107.24	0.3745		0.3746	−0.0001	380 min.	

Barium Chloride, 0.1 *molar*.

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
7	K	460.04	10.6238	30.33	9.8402	+0.7836	1.7479	41.44
	$\mathrm{M_{I}}$	46.30	1.0598		1.0605	−0.0007	0.108 amp.	
	$\mathrm{M_{II}}$	99.09	2.2686		2.2697	−0.0011	240 min.	
8	K	512.08	11.9214	57.06	10.4182	+1.5032	3.3519	41.46
	$\mathrm{M_{I}}$	35.77	0.8189		0.8193	−0.0004	0.122 amp.	
	$\mathrm{M_{II}}$	104.51	2.3911		2.3939	−0.0028	410 min.	
	$\mathrm{M_{III}}$	99.00	2.2673		2.2677	−0.0004		
9	K	507.37	11.7885	50.98	10.4500	+1.3385	2.9804	41.48
	$\mathrm{M_{I}}$	106.63	2.4411		2.4424	−0.0013	0.123 amp.	
	$\mathrm{M_{II}}$	101.06	2.3116		2.3149	−0.0033	360 min.	
	$\mathrm{M_{III}}$	90.10	2.0615		2.0638	−0.0023		
10	K	474.93	10.8589	30.31	10.1824	+0.6765	1.5019	41.50
	$\mathrm{M_{I}}$	103.15	2.3604		2.3628	−0.0024	0.065 amp.	
	$\mathrm{M_{II}}$	108.48	2.4821		2.4848	−0.0027	345 min.	
	$\mathrm{M_{III}}$	85.59	1.9574		1.9605	−0.0031		

Barium Chloride, 0.02 *molar.*

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
11	K	514.75	2.3897	54.95	2.1354	+0.2543	0.5321	44.31
	MI	110.70	0.5149		0.5142	+0.0007	0.034 amp.	
	MII	115.31	0.5362		0.5366	+0.0006	230 min.	
	MIII	89.89	0.4175		0.4175	0.0000		
12	K	499.37	2.3214	50.15	2.0864	+0.2350	0.4928	44.19
	MI	110.59	0.5142		0.5137	+0.0005	0.022 amp.	
	MIII[1]	86.12	0.4007		0.4000	+0.0007	275 min.	
13	K	493.42	2.2930	49.84	2.0601	+0.2329	0.4885	44.16
	MI	106.63	0.4957		0.4953	+0.0004	0.023 amp.	
	MII	109.52	0.5089		0.5087	+0.0002	260 min.	
	MIII	95.84	0.4451		0.4452	−0.0001		

Barium Nitrate, 0.1 *molar.*

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
14	K	244.30	5.2507	40.53	4.2970	+0.9537	1.9334	45.54
	MI	180.57	3.8058		3.8070	−0.0012	0.175 amp.	
	MII	199.75	4.2106		4.2212	−0.0006	165 min.	
	MIII	239.02	5.0368		5.0388	−0.0020		
	A	205.23	2.5491 2.2196	 39.325	3.5000	−0.9509		45.56
15	K	269.42	5.8130	43.89	4.7562	+1.0568	2.1540	45.47
	MI	174.74	3.6864		3.6840	+0.0024	0.178 amp.	
	MII	174.33	3.6760		3.6753	+0.0007	180 min.	
	MIII	183.50	3.8710		3.8685	+0.0025		
	A	218.25	2.5877 2.5527	 45.233	3.6497	−1.0620		45.48
16	K	268.51	5.7520	44.355	4.7270	+1.0250	2.0917	45.46
	MI	172.63	3.6428		3.6395	+0.0033	0.173 amp.	
	MII	147.53	3.1110		3.1098	+0.0002	180 min.	
	MIII	157.03	3.3132		3.3100	+0.0032		
	A	204.41	2.1725 2.9600	 52.44	3.2065	−1.0340		45.56
17	K	278.03	5.8841	46.49	4.8846	+0.9995	2.0301	45.54
	MI	168.20	3.5492		3.5488	+0.0004	0.168 amp.	
	MII	158.30	3.3329		3.3326	+0.0003	180 min.	
	MIII	153.30	3.2360		3.2345	+0.0015		
	A	205.69	2.4465 2.3988	 42.50	3.4451	−0.9986		45.42

[1] Portion MII was lost in this experiment.

Barium Nitrate, 0.02 *molar.*

Expt. No.	Portion.	Portion Analyzed.	Salt-Content.	Acid or Base Sol. Added.	Original Salt-Content.	Difference in Salt-Content.	Silver in Voltameter. Current. Time.	Transference Num.
18	K	197.50	1.0234	20.88	0.8242	+0.1992	0.4042	45.57
	MI	122.58	0.5744		0.5744	±0.0000	0.033 amp.	
	MII	134.06	0.6267		0.6269	−0.0002	180 min.	
	MIII	187.20	0.8143		0.8150	−0.0007 }		
	A	253.88	{ 0.7158		0.9149	−0.1991 }		45.70
			{ 0.6766	57.83				
19	K	207.34	1.0631	21.75	0.8660	+0.1971	0.4014	45.41
	MI	124.05	0.5773		0.5772	+0.0001	0.033 amp.	
	MII	141.65	0.6608		0.6610	−0.0002	180 min.	
	MIII	145.38	0.6781		0.6772	+0.0009 }		
	A	268.13	{ 0.7979		0.9971	−0.1992 }		45.68
			{ 0.6371	54.45				
20	K	201.18	1.0346	21.14	0.8382	+0.1964	0.3985	45.57
	MI	123.27	0.5630		0.5630	±0.0000	0.035 amp.	
	MII	121.00	0.5641		0.5640	+0.0001	170 min.	
	MIII	155.48	0.7240		0.7239	+0.0001		
	A	279.26	{ 0.8353		1.0329	−0.1976		45.85
			{ 0.6716	57.40				

The values of the transference numbers obtained (multiplied by 100) are summarized in the following table. At the foot of each column is given the mean of the values just above, and the average deviation of the separate values from this mean. To the final results in the case of the barium nitrate, the probable error, calculated in the usual manner, is appended.

Potassium Sulphate.		Barium Chloride.	
0.1 molar.	.02 molar.	0.1 molar.	0.02 molar.
49.41	49.68	41.44	44.31
49.33	49.59	41.46	44.19
49.19	49.58	41.48	44.16
		41.50	
49.31	49.62	41.47	44.22
0.08	0.04	0.02	0.06

Barium Nitrate.

0.1 molar.		0.02 molar.	
Cathode Values.	**Anode Values.**	**Cathode Values.**	**Anode Values.**
45.54	45.56	45.57	45.70
45.47	45.48	45.41	45.68
45.46	45.56	45.57	45.85
45.54	45.42		
45.50	45.50	45.52	45.74
0.04	0.06	0.07	0.07
45.50 ±0.02		45.59 ±0.08	

5. ACCURACY OF THE RESULTS.

The probable degree of accuracy of the results and the consequent reliability and value of the method employed may be next considered. It should be first stated that in the above tables all the determinations are recorded which were carried to completion after certain errors which were found to exist in the analyses were eliminated.

In the cases of potassium sulphate and barium chloride, there are two indications of the degree of accuracy of the results; first, the change in weight of the middle portions; and second, the variations in the transference-values calculated from the different experiments. In regard to the former, it should be stated that in the analyses of portions of the original solutions, variations from the mean salt-content of 0.0010 gm. in the more concentrated, and of 0.0005 gm. in the more dilute solution, were found to exist; so that only when the middle portions change by more than these amounts, do the changes have much significance. It will be seen that the changes in the M_I portions do not much exceed these amounts, except in the cases of experiments 2, 5, and 10; and in the first two of these experiments, the changes in the M_{II} portions are so small as to cause no hesitation in combining the changes of the M_I portions with those of the cathode portions. It will also be seen from the summary in the last table, that the average deviation of the separate transference values from the mean is in every case less than 0.2 per cent. Taking into account the possibility of an error of 0.1 per cent. in the determination of the original salt-content, it can, I think, be safely asserted that it is almost certain that the error in the mean transference values does not exceed 0.25 per cent.; in other words, the third figure cannot be in error by more than one unit. The probable error is, of course, much less.

In the case of the barium nitrate experiments, a more conclusive confirmation of the degree of accuracy of the results is furnished by a comparison of the cathode and anode values; for an error in the determination of the original salt-content of the solution or any error arising from mechanical loss in the analysis of the portions would affect these values in the opposite direction. In the case of the 0.1 molar solutions, the agreement is complete between the mean cathode and anode values. Taking into account, moreover, the smallness of the variations of the separate values of the mean, and the slight changes (0.2–0.7 mgm.) exhibited by the M_{II} portions, the final result (45.50) can, I believe, be regarded as almost surely accurate to 0.1 per cent. of its value. In the case of the 0.02 molar solution, the values calculated from the changes at the two electrodes differ by a little less than half a per cent. Attributing double weight to the cathode results, since an increase of the salt-content is produced by the base solution added at the anode, I adopt 45.59 as the most probable value. This may possibly be in error by 0.3 per cent., but is probably accurate to one-half that amount. Since at both concentrations, the final values are derived by a combination of the results of two independent methods which are liable to error in opposite directions, the probable errors given in the table are to be regarded as a measure, not merely of the variable errors, but probably of all errors involved.

These considerations show that the degree of accuracy attained with the help of the method described in this article is much greater than that which it has heretofore been found possible to secure. This arises mainly from the fact that the electrolysis could be continued until a much larger weight of salt was transferred. Thus, in my experiments, the quantities transferred were 180–260 mgms. in the 0.02 molar, and 700–1500 mgms. in the 0.1 molar solution, while, in Bein's determinations at corresponding concentrations, only 20–50 mgms. were transferred.

6. Comparison with Earlier Results.

Potassium sulphate was investigated by Hittorf[1] at 4°–12° at two concentrations, at about 0.5 and about 0.014 molar. The transference numbers found were 0.500 and 0.498, respectively. The differences from my values (0.4931 and 0.4962) are, therefore, not very large.

Barium chloride has been studied by various investigators with widely divergent results. Thus Hittorf[2] obtained the value 0.385 at 10°–20° for 0.04–0.06 molar solutions; while from Bein's results,[3] one finds by interpolation for 25° and 0.1 and 0.02 molar concentrations, the values 0.424 and 0.445, respectively. The latter differ by 2.2 and by 0.7 per cent., respectively, from those presented in this article (0.4147 and 0.4422). Hopfgartner's[4] determinations (at 15°) for a 0.1 molar solution, lead to the value 0.408 which is nearly as much below my result as Bein's is above it.

Barium nitrate has been investigated only by Hittorf,[1] who found 0.380 in 0.07, and 0.398 in 0.03 molar solution. These values differ very widely from my own (0.455).

These results make evident the great need of a repetition of much of the earlier work on tri-ionic salts.

7. Change of the Transference Numbers with the Concentration.

The effect of concentration, the study of which formed the main object of this investigation, may be now considered.

The transference number of potassium sulphate varies only from 0.4931 to 0.4962, or about 0.6 per cent., between the concentrations of 0.1 and 0.02 mols per liter. A little consideration will show that this change can be explained by assuming that 1.2 per cent. more of the dissociated part of the salt is dissociated into $K^{\cdot}$ and KSO_4' ions in the concentrated than in the dilute solution, it being further assumed, as a sufficiently close approximation, that the equivalent conductivities of all the ions involved are equal. But, since, according to Kohlrausch's measurements, the molecular conductivity between these two concentrations changes from 175 to 208 reciprocal ohms (and the dissociation from 64.5 to 77 per cent.), thus by 19 per cent., it is clear that by far the most important chemical change produced by the dilution is the dissociation of K_2SO_4 molecules and not of KSO_4' ions. Since the change in the transference number is so small, it may, however, be due solely to hydration of the ions.[1] Therefore, only the following negative conclusion is justifiable: *the concentration of KSO_4' ions*[2] *in a 0.1 molar potassium sulphate solution does not exceed a very few per cent. of the total concentration.* If these ions exist at all, they have a very much greater dissociation-tendency than the neutral potassium sulphate molecules.

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[1] Ostwald's Klassiker, No. 21, 58; or Pogg. Ann., 98, 29, 30.

[2] Ostwald's Klassiker, No. 23, 41; or Pogg. Ann., 106, 380, 381.

[3] Ztschr. phys. Chem., 27, 51.

[4] Ztschr. phys. Chem., 25, 138.

In the case of barium nitrate, the change (0.2 per cent.) caused by the five-fold dilution is still smaller, and does not exceed the probable experimental error. Therefore, *barium nitrate solutions up to 0.1 molar concentration contain in appreciable quantity only $Ba^{\cdot\cdot}$ and NO_3' ions and no complex ions formed by the combination of these.*

The difference in the transference numbers (0.4147 and 0.4422) of barium chloride at the two concentrations is very much greater than the differences just considered, amounting as it does to 6.6 per cent. The change is, moreover, in the opposite direction from that required by the assumption of the existence of $BaCl^{\cdot}$ ions in the more concentrated solution. In order to explain this behavior and the analogous one of strontium and calcium chlorides, Bein assumed a partial hydrolysis of the salt, basing this view on the disagreement of a single determination of the amount of calcium transferred with determinations of the chlorine transferred. This explanation can not, however, be correct, since the alkaline-earth hydroxides are known to be very strong bases; it is, moreover, entirely disproved in the case of barium chloride, by the substantial agreement (see § 6) of Bein's values, which are based on determinations of the chlorine transferred, with my results, which were obtained by determining the transferred barium. On the contrary, the behavior of these chlorides of the alkaline-earth metals is entirely similar to that of the halogen compounds of cadmium, though the anomaly is less pronounced; and, as far as I am able to see, it admits only of a corresponding explanation. In order to account for the fact that the sum of the transference numbers for the metal and chlorine is equal to unity, and for the change with the dilution, it is, namely, necessary to assume that *there are present in considerable quantity in the 0.1 molar solution of the alkaline-earth chlorides, complex negative ions formed by the union of one or more chlorine ions with one or more of the chloride molecules* (such ions, for example, as $BaCl_3'$ or $BaCl_4''$) and that these ions dissociate with increasing dilution.

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[1] Ostwald's Klassiker, No. 23, 41; or Pogg. Ann., 106, 378, 379.

[2] Thus the actual change of 0.6 per cent. would be entirely accounted for, if, with the equivalent weight of the $K^{\cdot}$ ions, migrate two molecules of water more than migrate with the equivalent weight of SO_4'' ions.

8. RATES OF MIGRATION OF THE BIVALENT IONS.

As Kohlrausch has pointed out, owing to the lack of exact transference values for tri-ionic salts, the Law of the Independent Migration of the Ions has not been satisfactorily confirmed in the case of bivalent ions; nor have their rates of migration, calculated with the help of that Law, been as accurately determined as have those of univalent ions, for the reason just mentioned, and also for the reason that the limiting value of the molecular conductivity of tri-ionic salts cannot be established with as great certainty, since a larger extrapolation is necessary.

With the help of the new transference numbers for potassium sulphate and barium nitrate, the equivalent conductivities of the SO_4'' and $Ba^{\cdot\cdot}$ ions can be calculated, if it be assumed that the values obtained for 0.02 molar solution at 25° would also hold true for extreme dilution and at 18°. That these assumptions will not give rise to an error greater than one per cent. is highly probable in view of the small changes between the two concentrations, 0.1 and 0.02 molar, and in view of the general principle that temperature has as a rule only a small effect on transference numbers. The calculation can be made in two ways, either by combining with my transference numbers the conductivities at extreme dilution of the $K^{\cdot}$ and NO_3' ions, which have been derived by Kohlrausch through a consideration of the transference numbers and the molecular conductivities of di-ionic salts; or by combining with them the limiting values of the equivalent conductivities of potassium sulphate and barium nitrate. The results so obtained for the SO_4'' and $Ba^{\cdot\cdot}$ ions can be then further compared with Kohlrausch's values which were derived by a combination of the two kinds of data last mentioned, without reference to the transference number of any tri-ionic salt.[1]

The three pairs of calculated values of the equivalent conductivities of the two ions are given below in the order in which they have just been referred to. The data used in the calculation are the transference numbers recorded above (0.4962 for K_2SO_4 and 0.4559 for $Ba(NO_3)_2$) and the following values of the equivalent conductivity expressed in reciprocal ohms at extreme dilution;[2] for $K^{\cdot}$, 64.8; for NO_3', 61.3; for K_2SO_4, 135.5; and for $Ba(NO_3)_2$, 119.3.

	I	II	III
SO_4''	65.8	68.3	69.7
$Ba^{\cdot\cdot}$	51.4	54.4	57.3

The difference between the three pairs of values are by no means inconsiderable. In the case of the $Ba^{\cdot\cdot}$ ion, indeed, the first and third methods of calculation give results differing by over 10 per cent. Aside from serious errors in the experimental data, these differences may be due to one or more of the three following causes: first, error in the conductivity values calculated for the univalent ions; second, error in the extrapolated values for the univalent conductivity at extreme dilution of the tri-ionic salts; and third, inaccuracy in the assumption that the transference numbers for potassium sulphate and barium nitrate at extreme dilution do not differ much from those found in 0.02 and 0.1 molar solution. It seems very improbable that any one of these three errors can be large enough to account for the divergences; a combination of them, however, may possibly do so. In the absence of definite information in regard to the matter, it seems best to adopt provisionally the values given in column II ($SO_4'' = 68.3$; $Ba^{\cdot\cdot} = 54.4$) which are the ones most directly derived from experimental data, and which are not far from the means of the other two pairs of values. These numbers give for the equivalent conductivities of potassium sulphate and barium nitrate, 133.1 and 115.7 respectively, while Kohlrausch's extrapolated values are 135.5 and 119.3.

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[1] Wied. Ann., 66, 805.

[2] These values are those given by Kohlrausch, Wied. Ann., 66, 795 and 819, 812 and 804.

In this connection it should be pointed out that in Kohlrausch's method of treatment of tri-ionic salts, the assumption involved that the conductivity of bivalent ions decreases with increasing concentration more rapidly than that of the univalent ions simultaneously present, is entirely inconsistent with the transference results on potassium sulphate and barium nitrate presented in this article. This is shown by the following transference numbers which are calculated for these two salts from his values for the separate ions at the various normal concentrations, which are stated below in the headline:

	0.1	0.05	0.02	0.01	0.001
K_2SO_4	0.571	0.557	0.534	0.522	0.499
$Ba(NO_3)_2$	0.397	0.414	0.434	0.446	0.468

It is certain from my results that any such change of the transference numbers with the concentration is out of the question in the case of these two salts. It ought to be added that Kohlrausch regarded his assumption only as a provisional one, having an empirical justification. That the results obtained with its help were at all satisfactory is probably due, first, to the fact that the compounds considered were mostly those of the halogens, and secondly, to the large errors in some of the transference numbers.

It is impossible to utilize the transference numbers of barium chloride, as was done with those of the nitrate, for the calculation of the conductivity of the barium ion, since the transference number of the former salt does change greatly with the dilution. It is of interest, however, to make the converse calculation so as to compare the transference number calculated for extreme dilution with that found at the concentrations investigated. Assuming as above, $Ba^{\cdot\cdot} = 54.4$, and according to Kohlrausch, $Cl' = 66.4$, the transference number for complete dissociation is found to be 0.450. (Even assuming Kohlrausch's much higher value (57.3) for the Ba¨ ion, the transference number becomes only 0.464). The value found for a 0.02 molar solution was 0.442, so that the change produced by further dilution is relatively small. At this concentration, therefore, the complex negative ions present in considerable quantity in more concentrated barium chloride solutions, are for the most part, dissociated.

In closing, I desire to state that the accuracy of the experimental results present in this article are to be attributed in large measure to the analytical skill and perseverance of my assistants, Mr. A. A. Blanchard and Mr. G. V. Sammet.

DETERMINATION OF POISSON'S RATIO BY MEANS OF AN INTERFERENCE APPARATUS.

BY J. R. BENTON.

POISSON proved that when a homogeneous isotropic body is extended in one direction, it must contract in the directions perpendicular to the extension, and that if the intermolecular forces are assumed equal in all directions, the contraction must amount to ¼ of the extension. Numerous experiments, embracing a great variety of methods, have shown that this contraction actually does take place, but that the ratio in which it stands to the extension—Poisson's ratio—is usually different from ¼. This is accounted for under the assumption of imperfect homogeneity; indeed the ratio varies greatly for the same material according to the manner in which it has been treated. Voigt,[1] experimenting on electrolytically deposited copper, where there is no reason to expect inhomogeneity, found the ratio to have almost exactly its theoretical value of ¼.

The methods of determining Poisson's ratio may be divided into two classes.

First, those which depend on a comparison of the elastic constants of the medium investigated. It can be shown that Poisson's ratio K satisfies the equation:

$$K = \frac{B}{A + 2B}$$

where A and B are fundamental elastic constants of the medium. A and B can be determined from the behavior of the medium with respect to two different kinds of deformations, such as extension and flexure. Thus extension and torsion were used by Kohlrausch and Loomis,[2] and by Baumeister[3] to determine K; flexure and torsion by Voigt,[1] Kirchhoff[2] and Okatow,[3] while Amagat[4] compared with other deformations cubical contraction under increase of pressure. Schneebelli[5] compared the velocity of torsional and longitudinal vibration of metal rods. Cornu[6] used an ingenious method in investigating Poisson's ratio for glass; one piece of glass was slightly bent by means of weights, and another piece was laid on it; the resulting interference bands had the form of hyperbolas, and it can be shown that the tangent of the angle between the asymptotes of the hyperbolas and the axis of the glass plate is equal to Poisson's ratio.

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[1] W. Voigt: Berliner Sitzungsberichte, 1884, p. 961; 1884, p. 1004.

[2] Poggendorff's Annalen, Band 141, p. 502, 1870.

[3] Wiedemann's Annalen, Band 18, p. 578, 1883.

Second, Poisson's ratio may be determined by measuring the contraction at right angles to the direction of the extension, and comparing it with the extension. The former of these quantities is very small, and has to be measured indirectly, unless the stretched body is a very thick rod, in which case larger forces than are usually available have to be applied to produce an appreciable extension. The problem reduces itself, therefore, to that of the measurement of a very small distance.

The first determination, carried out by Cagniard de la Tour[7] to test Poisson's theoretical result, was made by stretching a wire contained in a narrow tube filled with water. The contraction of the wire was calculated from the change of level of the water. A similar method was employed by Wertheim,[8] who made important investigations of Poisson's ratio; he filled a hollow cylinder, communicating with a capillary tube, with water; when the cylinder was stretched, the change of its volume could be determined from the change of level of the water in the capillary tube, and from this Poisson's ratio was obtained. Both these methods were unsatisfactory, because the apparatus acted like delicate thermometers, a very slight change of temperature of the large mass of water making a great difference in its level in the narrow tube.

[1] W. Voigt, Wiedemann's Amalen, Band 15, p. 497, 1882.

[2] Pogg. Annalen, Band 108, p. 369, 1859.

[3] Pogg. Annalen, Band 119, p. 11, 1863.

[4] Comp. Rend., 21, July, 1884.

[5] Pogg. Annalen, Band 140, p. 589, 1870.

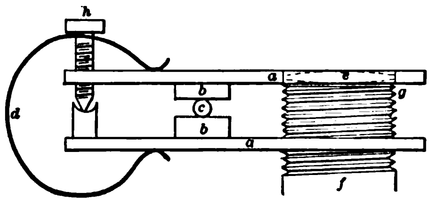
[6] A. Cornu, Comptes Rendus, Tome 69, p. 333, 1869.

[7] Ann. Chim. Phys., Tome 36, p. 384, 1827.

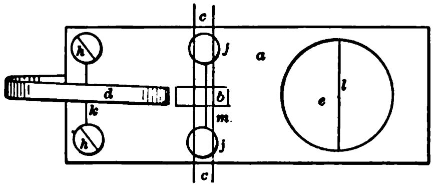
[8] Ann. Chim. Phys., 3 ser., Tome 23, p. 52.

Measurements by means of the microscope have been made by Mallock,[1] who determined the change in distance between points marked on a rod, when the rod was bent. Direct measurement of the contraction has been made in cases where the deformation was very great; thus Röntgen[2] determined Poisson's ratio for caoutchouc by stamping a circle on a stretched band; when the tension was removed the circle became an ellipse whose axes furnished the necessary data for the determination.

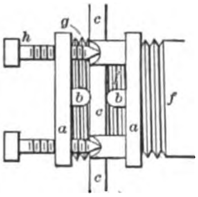
At the suggestion of Professor Voigt, I undertook the measurement of the contraction by means of interference bands. The experiments were made in his laboratory in the University of Göttingen.



View from above.



Front view.



Side view.

Fig. 1.

The interference of light has been already used to determine Poisson's ratio. Stromeyer and Kennedy[3] made use of it to measure the contraction of thick metal bars which were stretched in a testing machine. My apparatus is designed for use where such large forces are not available.

After making attempts with numerous variations of the apparatus, the following was found to give the most satisfactory results. *a*, *a* (Fig. 1) were plates of brass, on which the rounded bits of steel *b*, *b* were soldered, and firmly pressed against the wire *c* by means of the spring *d*. One plate contained a lens *e*, of slight curvature, the other a tube *f*, having a screw thread so that the distance of the glass plate *g* in its end from the lens could be adjusted. The back side of the glass plate *g* was blackened. By means of the screws *h*, *h* it was possible to set the plate perpendicular to the axis of the lens; in which case interference rings appeared, provided the distance between lens and plate was not too great. If the wire contracted, the distance became less, and new rings appeared. If sodium light is used, each new ring corresponds to a difference of distance of 294.5×10^{-6} mm., the half wave length of the light. This difference is not, however, itself the contraction of the wire, but the latter must be deduced from it when the distance of the wire and the center of the interference rings from the axis are known, around which the brass plates move. This axis is simply the line passing through the points of the screws *h*, *h*. In order to measure the distance from this axis, I ruled the fine lines *k*, *l* and *m* and measured accurately the distances *kl* and *km*, once for all. Then in any particular case the distances from *l* to the center of the rings, and from *m* to the center of the wire (seen through the holes *jj*) were measured by means of a microscope, and added to or subtracted from *kl* and *km*.

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[1] Proc. Roy. Soc., vol. 29, p. 157, 1879.

[2] Poggendorff's Annalen, Band 157, p. 601, 1876.

[3] Proc. Roy. Soc., vol. 55, pp. 373-383, 1894.

The wire was fastened above a table *a* (Fig. 2) and hung through a hole in it. *b* was a strong piece of iron. Underneath, the hook *d*, carrying the scale pan *e*, hung from a loop in the wire. A stiff iron rod *f*, free to move round the horizontal axis *g*, passed through a hole in the rod *h* and carried a weight *l*. The purpose of the weights *e* and *l* was simply to hold the wire tight, and to prevent *f* from slipping in the hole *h*. The weight by which the tension of the wire was produced, was applied to the end of *f*. The weight *i* wasplaced on a scale pan, which could be lowered by the windlass *k* so as to the rest on *f*, or raised from it; the purpose of this arrangement being to avoid jars in changing the weights. The interference apparatus was at *m*: in front of it was a Bunsen bürner

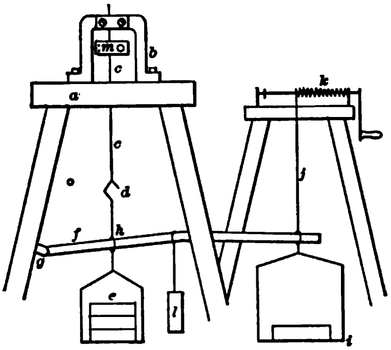

Fig. 2.

(not shown in the figure), in which a bead of Na_2CO_3 was held, and a microscope (also not shown), with which the rings were observed. The angle between the incident and the reflected ray was very small.

Each wire, after being fastened in the iron *b*, was heated to dull redness under a small load, by means of a Bunsen burner, in order to insure its hanging straight. Then it was left a day or two under a somewhat greater load than the one to be used in the experiments, after which the measurements were made.

The interference apparatus was placed on a wire, and the screws *hh* (Fig. 1), and the tube *f* so adjusted that the plate *g* was perpendicular to the axes of the lens, and very near to it, but yet not so near as to come into actual contact with it when the wire contracted. The cross-hairs of the microscope were set at first on the center of the rings which appeared under these conditions. Then the microscope was clamped in position, and the micrometer screw-head was turned until the intersection of the cross-hairs was on the tenth ring above the center. Here five readings of the micrometer were made, then the cross-hairs were brought on to the tenth ring underneath, where five readings were taken; then five readings were taken again on the tenth ring above. The difference between the average reading above and below gives the diameter of the tenth ring in terms of the divisions on the screw-head. Then the tension was brought to bear on the wire, the number of new rings counted, and the diameter of the tenth ring under these conditions was measured. Finally the tension was removed, another measurement of the diameter of the tenth ring was made, and also its difference from the diameter of the ninth ring and from that of the eleventh determined. The difference in diameter between the tenth ring with and without tension, divided by the difference in diameter between the tenth ring and the ring next to it, gives the fraction which must be added to the number of new rings in order to determine the change of distance between the plate and the lens. Suppose, for example, that the diameter (in terms of the divisions on the screw-head) of the tenth ring is 18.221 with tension, 18.005 without tension; that the average of the difference in diameter between the ninth and tenth, and between the tenth and eleventh rings is 0.920; and that 4 new rings have appeared, then the distance through which the lens and plate have approached each other is

$$294.5 \times 10^{-6} \times \left(4 + \frac{18.221 - 18.005}{0.920}\right) = 1247 \times 10^{-6} \text{ mm.}$$

After making two such determinations at different places on the wire, it was loosened, turned through 90°, fastened again, heated to dull redness, and left hanging under a heavy load for a few hours. Then similar determinations were made at two different places on the wire, so that for each wire four determinations were made. The results given below are the averages of four such determinations each. The distance of the wire and rings from the screws *hh* (Fig. 1) was measured as described before; the weight *i* (Fig. 2) and the scale pan were weighed in a balance; the distance of the wire and the weight from the axis *g* were measured with a millimeter scale; and the diameter of the wire was measured with accurate calipers, the mean of six measurements being taken. From these quantities the contraction of the wire due to unit tension can be calculated.

Poisson's ratio is obtained by dividing this contraction by the extension due to unit tension. The last-named quantity was determined by measuring, with a micrometer, the vertical distance through which a needle point fastened to the end of the wire moved when weights were hung on the wire. For this purpose a 3-meter length of wire was used.

The values of Poisson's ratio found for a number of wires are given in the following table:

Substance.	Diameter.	Poisson's Ratio.	Mean Value.
Steel.	0.685 mm.	0.276	
	1.405	0.275	0.2755
Iron.	0.948	0.294	
	1.578	0.282	0.288
Copper.	1.390	0.337	
	1.728	0.345	0.341
Nickel.	0.963	0.375	
	1.490	0.271	
Brass.	0.787	0.328	
	1.498	0.334	0.331
Nickelin.	0.978	0.406	
	1.397	0.399	0.403
German Silver.	1.005	0.313	
	1.592	0.429	
Bronze.	0.902	0.414	
Brass containing much copper.	0.996	0.300	

The highly unsatisfactory discordant results for nickel appear to be due to some difference in the physical condition of the two wires. I found that their specific gravities were somewhat different. Of course the experiments were repeated, as soon as the discrepancy was found, but the same results were obtained.

The difference between the two values for German silver is due to difference in the composition of the alloy for the two wires.

THE USE OF THE BICYCLE WHEEL IN ILLUSTRATING THE PRINCIPLES OF THE GYROSCOPE.

By Charles T. Knipp.

IN the gyroscope as ordinarily made the true oscillatory motion of the axis is not shown except for extremely slow speeds of the fly wheel and then only for a few seconds. The oscillations are damped by the friction of the supports, causing the precessional motion to become steady.[1] The form of the gyroscope that best shows the true motion of the axis is a gyroscopic pendulum of considerable length. When in the form of the balanced gyroscope, where the balance can readily be destroyed by shifting the weight, thus coverting it into a gyroscopic pendulum of short length, the ordinary construction enables the oscillations to be seen only for slow speeds and short intervals; while in the top they are, in the ordinary form of apparatus, never visible.

The study of the phenomena peculiar to the gyroscope is greatly simplified, and at the same time brought within the reach of all, by using an ordinary bicycle wheel as the fly-wheel. So simple is the apparatus and yet so effective that it was thought well to call attention to some of the salient points.

The bicycle wheel works equally well as a gyroscopic pendulum, as a balanced gyroscope, and as a top. It is readily mounted by any one who has access to a shop in which iron work is done, or any bicycle repair shop. The wheel is taken from the front fork without disturbing the adjustment of the ball bearings. A $\frac{3}{8}$-inch iron gas pipe nine inches long is tapped out at one end and screwed on the axle of the wheel. The other end of the gas pipe, which is threaded to receive an ordinary connector, is slitted with a hack saw. The connector acts as a compression nut enabling the axis to be extended to any length by inserting an iron or brass rod.

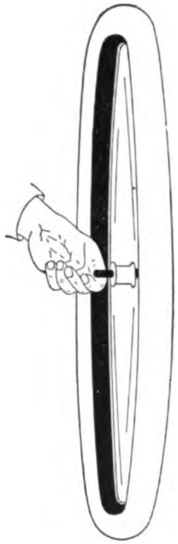

Fig. 1.

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[1] Merritt, Phys. Rev., vol. 14, p. 336, 1897.

Fig. 1 shows the wheel as when first taken from the bicycle. The axle extends beyond the hub far enough to give plenty of room for support. When spun and held as shown it furnishes a striking example of the familiar toy gyroscope. It is very positive in its precessional movements and seeming defiance to the laws of gravitation. In this form it is interesting to study its erratic movements when disturbed. This is best done by firmly grasping the ends of the axle with both hands and endeavoring to tilt the axle quickly while the wheel is turning. No doubt this simple experiment with the bicycle wheel is familiar to all.

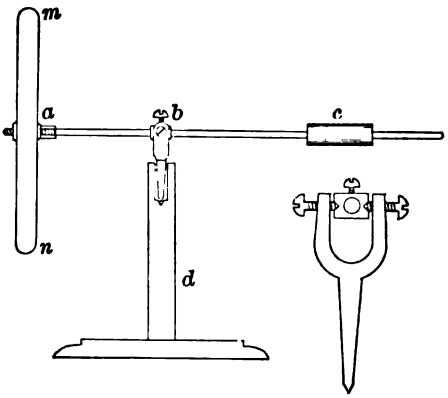

Fig. 2, Fig. 2a.

The balanced gyroscope is shown in Figs. 2 and 3. The mounting shown in Fig. 2 is formal, and brings out the points in question better than the manner of mounting shown in Fig. 3. The $\frac{3}{8}$-inch gas pipe that is fastened directly to the axle of the wheel is not shown. The wheel *mn* is counterpoised by a weight *c* which may conveniently be a piece of lead pipe. Fig. 2a shows in detail the manner of support.

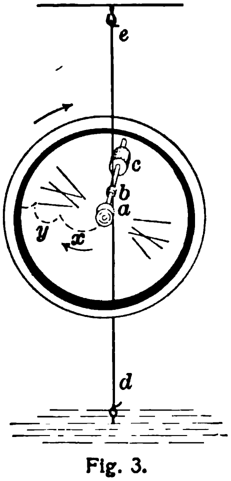

Fig. 3.

In Fig. 3 the gyroscope is simplified by supporting it from a suitable hook or a chandelier by a stout cord. To steady the apparatus the cord is continued to the floor and tightly tied to a screw-eye *d* placed directly beneath the hook *e* in the ceiling. This form of support is not as rigid as that in Fig. 2, yet the motion of the gyroscope is not appreciably affected because of this.

When the weight *c* is adjusted so that the gyroscope is balanced, there is no tendency for the axis *ac* to change its direction when the wheel is given a rotatory motion. However, if the weight *c* is moved along the axis the center of gravity of the system is changed and the gyroscope becomes a gyroscopic pendulum; if *c* is moved toward *b* it becomes a gyroscopic pendulum with its center of gravity displaced towards the fly-wheel. If the fly-wheel is given a rotatory motion, then if the weight *c* is released and the instrument left to itself precessional motion will begin accompanied by marked oscillations. If the direction of rotation of the fly-wheel is as indicated by the arrow, *i. e.*, negative when looking along the axis from the point of support *b*, the trace of the axis of the gyroscope will be the cycloidal path *xy*, and its direction (looking down) is positive. The size and frequency of the oscillations depend upon the speed of the fly-wheel, becoming smaller and more frequent as the speed is increased. It might be well to state that the rotation is imparted to the wheel by inserting a small rod or wire nail between the spokes where they cross near the hub, and turning the wheel as by a crank of short radius. Thus a large angular velocity can be imparted to the wheel; though this is much smaller than the angular velocity of the fly-wheel of the ordinary gyroscope. Even at this comparatively small speed of rotation the gyroscope maintains the plane of its axis fairly well fixed for some time. The oscillations *xy* of the axis are noticeable until the gyroscope has precessed 6 or 7 complete revolutions. If *c* is moved away from the support we are led from geometrical considerations to expect that the precessional motion will be in the opposite direction, with the cusps of the cycloidal path pointing downward. The position of the gyroscope, cycloidal path, etc., when *c* is moved out, is given by *inverting* Fig. 3.

In Fig. 4 is represented the gyroscope in the form of a gyroscopic pendulum of considerable length. In this form, probably better than in any other, is shown the resistance offered to any change in the direction of the axis. Especially is this noticeable if the rod *af* is slightly flexible.

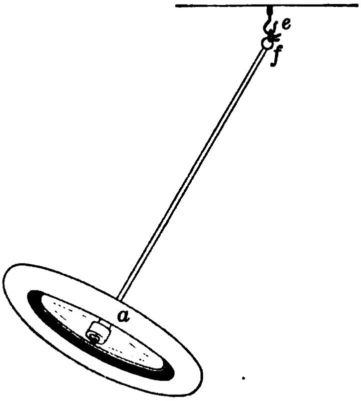

Fig. 4.

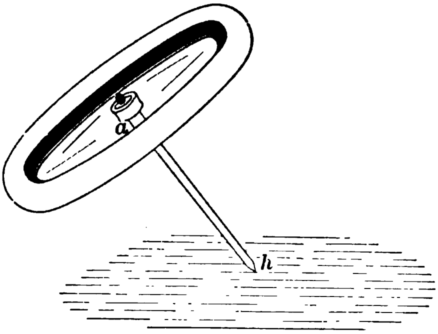

Fig. 5.

To make the apparatus assume the form of a top it is only necessary to loosen the compression nut, withdraw the rod, and insert in its place a wooden point. The top is shown in Fig. 5. If the bearings are free, the axis *ah* will not turn. It may be interesting to know that even in this form the oscillations are noticeable, but for no longer than one revolution of precessional motion.

This form of gyroscope has several advantages over the ordinary form. The large diameter of the wheel and consequently small angular velocity make the precessional and oscillatory motions slow, thus enabling the same, especially the latter, to be followed more easily. The friction at the hub, in proportion to the masses in motion, is very much less in the bicycle wheel gyroscope because of the ball bearings. The friction at *b* (Figs. 2 and 3) is but little felt, since the lever arm *ab* is quite long. Still another advantage is its simplicity. It is within the reach of every one who possesses a bicycle. It cannot fail to attract the person who seeks merely for a qualitative explanation as well as those who wish to apply more rigid analytical methods, and it is for these reasons that the foregoing is submitted.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, June, 1900.

AN AUTOMATIC TEMPERATURE REGULATOR.

By Chas. T. Knipp.

DURING the past two years while conducting some experimental work it was necessary to maintain a piece of apparatus at constant temperatures for a day or more at a time. The range used was from room temperature to 380° C. The heating was by means of the electric current, the source of which was a 110-volt Edison dynamo. This current fluctuated under a varying load so that the heat from the coils was unsteady. Even if the current were steady some regulating device would be necessary if it were desired to keep the temperature constant for some time.

To this end an automatic regulator was devised. Two CuFe thermostats *ab*, *ab′* were clamped with their backs together as shown in Fig. 1. *MN*, the main support, carried at its upper end an arm *Ma* from which at *a* the thermostat was suspended by pivots. The lower end of the arm *ab′* was fastened by pivoted connections directly to the support *MN*, thus leaving the lower end of *ab* free to

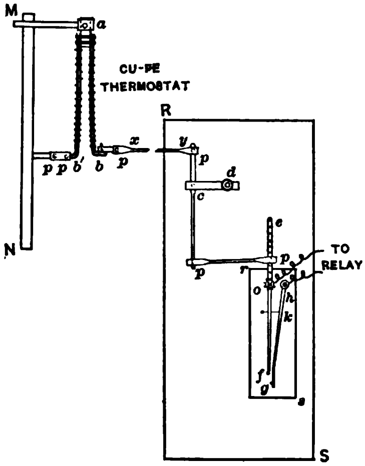

Fig. 1.

move in the plane of the paper, its motion being that due to both branches of the thermostat. This motion communicated by an aluminium rod *xy* to a system of pivoted aluminium levers mounted on a vertical board *RS*. The first lever had its fulcrum on a movable support at *c* which was capable of adjustment up and down by means of a thumb-screw at *d*. The motion of the lower end of this lever was communicated to another lever *ef*. This lever was mounted on a separate board *rs*, and both lever and board were pivoted concentrically at *o* to *RS*. The lower end of *ef* terminated in a platinum ring. Another lever supported on *rs* and pivoted at *h* was held lightly against a stop *g* by a delicate spring at *k*. The lever *hg* was flattened at its lower end and carried a platinum surface on which *f* played. All of the joints *p* were delicately pivoted needle points. The amount of motion at *f* could be varied through a considerable range by adjusting the length of the levers *op* and *cp*. Wires led from *o* and *h* to a relay which in turn operated an ordinary sounder that controlled a part of the heating current.

The heating coils were in two sections ; one to heat the oven to within 5 or 10 degrees of the temperature desired, and the other to furnish the heat that was needed to keep the temperature constant by means of the regulator. By swinging *rs* about *o* the two platinum contacts could be adjusted to correspond to any temperature.

The oven consisted of a sheet iron box lined both inside and out with ¼-inch asbestos. To still further guard against radiation the oven was surrounded with an asbestos-lined wooden jacket, leaving an air-space of about two inches between the two. Windows of heavy plate glass were placed in the opposite walls of the oven and jacket. The thermostat was placed within the oven and about one inch from one of the walls. The rod *xy* extended through an opening in both walls, communicating the motion of the thermostat within to the system of levers without. Care was taken to have this opening as small as possible, yet to insure freedom of motion. The heating coils were placed at the bottom, and the bulb of the thermometer extended down to about the center of the oven. No attempt was made to screen the direct radiation from the coils. The windows enabled the coils to be seen and overheating was thus avoided.

Two curves were platted. The first (Fig. 2) shows the variation of the temperature of the oven when the apparatus was adjusted for 25, and the second (Fig. 3) when adjusted for 375 degrees centigrade. At the low temperature the first section of the heating coils was dispensed with, since the temperature was but a few degrees above that of the room. At first the variation in temperature was nearly 1 ½ degrees, but in the course of fifteen or twenty minutes it reached a fairly steady condition, it being some less than .5 of a degree. By better adjustment, no doubt, a less variation could have been obtained. At the high temperature both sections were used. The resulting curve is more broken (Fig. 3); it falls from a maximum in much less time than at the low temperature. Both curves are steeper while heating than while cooling, indicating that the regulating coil was too hot, *i. e.*, it took longer to cool through a given range of temperature than to heat through the same range. The regulation at the high temperature, after the lapse of some minutes, was within a half degree.

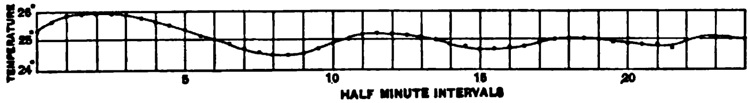

Fig. 2.

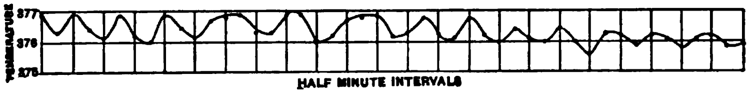

Fig. 3.

The essentials to success in this method of automatic temperature regulation are that the friction must be reduced to a minimum by using needle point bearings, and that the platinum contact be kept bright. An ordinary gravity cell with considerable resistance in the circuit will operate the relay.

Physical Laboratory, Cornell University.

THE SPECIFIC INDUCTIVE CAPACITY OF DIELECTRICS IN A MAGNETIC FIELD.

By Edward Coleridge Roberts.

THE experiments of Faraday and Kerr on the behavior of polarized light in passing through various media, when these are in a magnetic field, or subject to dielectric strain, make it seem possible that the presence of a magnetic field may have some effect on the specific inductive capacity of a dielectric. The following experiments were undertaken in order to discover if possible whether such an effect exists.

Although the method of attacking the problem was varied, the whole procedure was based on the fact that if a condenser be charged and insulated, any change in the specific inductive capacity will manifest itself as a change in the potential difference between the coatings.

The dielectrics studied (glass, hard rubber, and vulcanite) were used in the form of small condensers. Sheets of tinfoil 5.3 cm.^{2} were fastened on opposite sides of a plate of the dielectric, which was in each case about 20 × 25 cm., thus making the leakage path rather long. In the case of glass the whole condenser was covered with shellac to further decrease the leakage. The direction of the electric strain was parallel to the lines of magnetic force in nearly all cases.

The magnet used had 2,300 turns on each arm, and was capable of maintaining a field of 1,500 lines per cm.^{2} across an air gap of 3.5 cm., the pole pieces being 5.3 cm. square. This wide air gap was made necessary by the fact that the condenser and its connections had to be enclosed in a metallic shield, which was grounded, in order to protect them from induced charges set up by the windings of the magnet. It was found necessary to extend the shielding over the electrometer also, as otherwise the false deflections would render any accurate readings impossible.

In the first method the quadrants of the electrometer used to measure the potential of the coatings were kept charged to about 300 volts.[1] One side of the condenser was grounded and the other connected to the needle of the electrometer, and at will to one pole of a battery of 100 water cells, the other pole of which was grounded. The test as to whether proper conditions of screening had been arrived at was that no deflection should be observable when the field was established through the uncharged condenser. Condenser and needle were then charged as mentioned above, and insulated. The magnetic field was then established, both directions of field being obtainable by means of a reversing switch placed in the circuit. If now a deflection of the electrometer were observed, coinciding in time with the presence of the field, it would indicate that some change had taken place in the dielectric, presumably a change in the specific inductive capacity. When such measurements were made in the case of hard rubber and vulcanite the change, if it existed, was so small as to be unobservable. A method for glass based on the rate of discharge was tried, but the results were inconclusive. The sensitiveness of the electrometer was such that a variation of potential, and therefore a change of specific inductive capacity, by an amount equal to 1/500 of the whole could have been detected.

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[1] This difference of potential was furnished by a battery of 600 water cells.

The second method of procedure was as follows: A very constant alternating current was obtained by driving a small generator from a storage-battery-driven motor, and exciting the fields of the generator from another section of storage battery. The terminals of the generator were closed by a circuit containing one of the condensers used in the previous work, and a resistance consisting of 5 m. of lead pencil mark on ground glass. The condenser was as before held between the poles of the magnet, and it and its connections were as before enclosed in metallic shields. The potential difference across the resistance was measured by means of the electrometer, used idiostatically.

The amount of current which could flow in this circuit depended, among other things, on the specific inductive capacity of the dielectric. If, therefore, this was changed by the action of the magnetic field, the current would suffer a similar change, and this would be indicated by the variation of potential across the resistance. Inasmuch as the coatings were joined by a metallic conductor, no difficulty was experienced in getting rid of induced charges. Each of the condensers used in the previous work was studied by this method, but in no case was any change of potential evident when the magnetizing circuit was closed. The accuracy which the method permitted precluded a change in the specific inductive capacity greater than 1/200.

The third method of study, which seemed to be more accurate than either of the other two was applied to the rubber plate only. Two condensers of the same size as before were formed on the same plate, a little distance apart. The plate was so placed in the field that one was in the most intense part, and the other removed from that part by about twice the width of the air gap between the poles. The two coatings on one side were connected and grounded. Wires from the two coatings on the opposite side were connected to the opposite quadrants of the electrometer, and were so arranged that both could be charged to a fairly high potential and insulated. The electrometer needle was charged by a spark from an electrophorous. The shielding arrangements were the same as in the other cases, and much more perfect results were obtained from the fact that the electrometer was connected to two like coatings, which were subject to the same sources of electrostatic disturbance.

If the presence of a magnetic field altered the specific inductive capacity, such a change would differ in amount in the two condensers, because the field strengths were different in the two cases, and this would have been shown by a relative change of potential between the two like coatings. This test when applied led, like the preceding ones, to negative results. Experiment showed that a potential of 1/50 volt was observable when the electrometer was used in this manner. Since the potential of the charge was about 70 volts the smallest observable change would have been 1/50 of 1/70 of the whole, or 1/3500, and this would have been the relative change of specific inductive capacity due to the field. This method therefore shows that if the suspected effect exists its value is less than 1/3500 of the whole, assuming that the magnetic field at the second condenser is small.

These experiments were merely preliminary ones, and were undertaken principally for the purpose of getting a measure of the general nature and difficulty of the problem. To get results of any real value much greater refinements of measurement, and more perfect means of eliminating disturbances, must be employed. It has seemed worth while to call attention to the work now only because the subject is one in which, so far as the writer is aware, very little work has been done.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, November, 1900.

NOTE ON THE EFFECT OF TENSION ON THE PERMANENT TORSION OF A WIRE.

By J. R. Benton.

WHEN a wire hangs free and weights are fastened to its lower end, it has been observed that a change of the weights causes the wire to twist in one direction or the other, and to come to rest at a different position. An investigation of these phenomena has been made by Himstedt.[1]

It is curious to note that similar changes in the permanent torsion of a wire are caused by increasing its tension when it is clamped fast at top and bottom, as well as when it hangs free. Such changes appear to be due to inhomogeneity and internal strains of the wire; yet great precautions to get rid of these causes failed to prevent the change in torsion from occurring. Each wire was heated twice to dull redness under the greatest safe load, and then left hanging free under a considerable load for at least twenty-four hours, before it was clamped at the bottom.

The observations were made in connection with an investigation of the dependence of the modulus of torsion on tension. Details of the arrangement and treatment of the wires will be found there.

The following table gives (in degrees of arc) the torsion of various wires, when different weights were hung on them. The wires were each about three meters long.

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[1] Wiedemann's Annalen (3), Band 17, p. 701.

Weight in kgs.	2	4	5	6	7	8	10	11	14	15	18	20	23	25	30
Steel diam. 1.0 mm.							−0.9°			−0.6°		−0.5°		−0.4°	−0.4°
" " 1.5 "							−0.8°			−0.7°		−0.4°		−0.3°	−0.2°
Iron " 0.8 "	−0.1°	+0.1°		+0.2°		+0.4°	+0.5°								
" " 1.5 "							−0.4°			−0.2°		−0.1°		−0.1°	−0.1°
Copper " 0.8 "	−0.5°	0°		+0.2°		+0.3°	+0.3°								
" " 1.2 "	−1.2°		−0.8°				−0.5°			−0.1°	−0.1°				
" " 1.8 "							−0.2°			0°		0°		+0.2°	+0.3°
Nickel " 1.0 "	+0.1°		+0.4°				+0.5°			+0.5°	+0.6°				
" " 1.5 "							−0.5°			−0.4°		−0.3°		−0.2°	−0.2°
Brass " 0.8 "	−0.9°		−0.8°			−0.8°		−0.7°	−0.7°						
" " 1.5 "					0°		+0.1°			+0.1°		+0.2°	+0.2°		
Nickelin 0.8 "	0°		+0.2°				+0.2°			+0.3°	+0.3°				
" 1.5 "							−0.6°			−0.5°		−0.7°		−0.3°	−0.3°
Ger. silver 1.0 "	−0.1°		+0.3°				+0.3°			+0.5°	+0.5°				
" 1.5 "							−0.6°			−0.5°		−0.4°		−0.3°	−0.3°
Bronze 0.9 "	−1.0°	−0.7°		−0.5°		−0.3°	−0.2°								

NEW BOOKS.

A Treatise on the Kinetic Theory of Gases. By S. H. BURBURY, M.A., F. R. S. Pitt Press, Cambridge. 1899.

Once more we have before us an attempt to put the kinetic theory of gases on a more secure basis. In a modest volume of 157 pages, Mr. Burbury has made an effort to examine more carefully the assumptions, tacit or otherwise, and where these are faulty or not properly carried through to their logical conclusion, to correct the formulæ. And these are not easy tasks. The problem of the subject stated briefly is as follows: To find the circumstances of the motion of a dynamical system consisting of an infinite number of separate bodies each of which may have any number of degrees of freedom. The problem is of course not even theoretically soluble without an exact specification of the forces and the initial circumstances of the motion, but by making certain assumptions we are able to arrive at some results concerning the motion of the system. It is on these assumptions that the main interest of Mr. Burbury's volume centers. Delicate questions in the theory of probability have to be negotiated and even when these are settled the mathematical pitfalls are as numerous as those encountered in finding a rigorous proof of Taylor's theorem.

The main idea of the author is best given in his own words. He says that the kinetic theory of gases "has always been treated on a certain fundamental assumption, namely, that the molecules of a gas are, as regards their relative motion, *independent* of one another. As a consequence, we may say as the expression, of that independence, the law of distribution of momenta assumes the exponential form e^{-hQ}, and, so far as concerns translation velocities,

$$Q = \Sigma m\,(u^2 + v^2 + w^2),$$

m being mass, and u, v, w component velocities. From this independence and from this form of Q are deduced Boltzmann's theorems, namely the H theorem, and that of the equality of mean kinetic energy, for each degree of freedom.

I propose to give to Q the more general form of a quadratic function, namely,

$$Q = \Sigma m(u^2 + v^2 + w^2) + \Sigma\Sigma b(uu' + vv' + ww').$$

Here b is a negative function of the distance r at the instant considered between the two molecules whose velocities are *u*, *u'*, etc., which function is inappreciable except for very small values of *r*. . . . The consequence of attributing to *Q* the proposed new form is, that molecules near to each other have on average a motion in the same direction. They tend to form streams."

In order, then, to clear away doubts at the outset, the author examines the conditions under which the previous form of *Q* has been established. There is condition *A*, in which the chance of any molecule having a velocity between given limits is independent of everything else but that velocity and, in particular, independent of the motions and positions of the other molecules; and condition *B*, in which the chance is not independent of these other circumstances. From another point of view the question is this. Can the ordinary kinetic theory, in which we search for a stationary motion, be shown to include the case where the molecules have a sensible effect on one another? If not, in what respects must the theory be altered? The condition *A* leads to the Maxwell distribution. To what distribution will condition *B* lead?

The earlier part of the book is therefore devoted to the examination of the limitations of the results obtained under condition *A*, and it is shown that stationary motion is impossible with the first form of *Q* unless the molecules are independent. After this destructive criticism the author proceeds to examine the second form of *Q* in the light of condition *B*. Stationary motion becomes possible even when the molecules do influence one another provided the coefficients *v* fulfill certain conditions which may be considered probable. In gases under ordinary conditions, Mr. Burbury believes that these coefficients are quite small so that no sensible error will be made by omitting them. Thus condition *A*, which theoretically applies only to an infinitely rare medium, is practically very little in error unless the gas becomes very dense. An interesting conclusion is that under condition *B*, the molecules tend to form streams and the author sees in this tendency a suggestion as to the manner in which condensation takes place under increased pressure. The argument by which he arrives at these conclusions is not, however, altogether convincing.

To follow Mr. Burbury through the various steps to the last chapter which treats of the second law of thermodynamics would lead us outside the scope of this review. For these the reader is referred to the book itself. As a mathematical treatise it will not be found to be easy reading, partly owing to the nature of the subject and partly owing to the conciseness of the author's style. An acquaintance with the earlier books of Watson, Boltzmann or Meyer will be found to be necessary for understanding his position and indeed the details of his arguments. The book thus appeals mainly to specialists and it would be ungenerous to point out its defects as a text-book. It is, in fact, the compilation of the valuable work which Mr. Burbury has been doing for some years past and as such will be welcomed by those who take an interest in the subject and appreciate the value of Mr. Burbury's services to it.

ERNEST W. BROWN.

Introduction to Physical Chemistry. By JAMES WALKER, D.Sc., Ph.D., Professor of Chemistry in University College, Dundee.

There are few teachers of physical chemistry who have not been asked what book ought to be read before the larger text-books are undertaken? And everyone has doubtless felt the lack of any adequate work to recommend at this stage of development. It is true that the little book by Reychler on the elements of physical chemistry is both clear and concise, but it is a text-book, and a text-book as such is not what is desired at the beginning. The students of chemistry wish first to look at some length into certain interesting phases of physical chemistry, and then to take up a systematic treatment of the subject.

Professor Walker has evidently felt the need referred to and has endeavored to meet it. To quote from his preface, "This book makes no pretensions to give a complete or even systematic survey of physical chemistry. Its main object is to be explanatory. I have found in the course of ten years' experience in teaching the subject, that the average student derives little real benefit from reading the larger works which have hitherto been at his disposal, owing chiefly to his inability to effect a connection between the ordinary chemical knowledge he possesses, and the new material placed before him. He keeps his everyday chemistry and his physical chemistry strictly apart, with the result that instead of obtaining any help from the new discipline in the comprehension of his systematic or practical work, he merely finds himself cumbered with an additional burden on the memory, which is to all intents and purposes utterly useless. This state of affairs I have endeavored to remedy in the present volume by selecting certain chapters of physical chemistry, and treating the subjects contained in them at some length."

The origin of the Atomic Theory is traced and the methods of determining Atomic Weights. The development of our conception of Element, Atom and Molecule is followed up, and a table of the most accurate atomic weights is given. The Periodic System is treated both from the relation between physical properties and atomic weights, and chemical properties of the atoms and their relative weights. Chapters on Solubility, Fusion and Vaporization are followed by a clear and concise discussion of the Kinetic Theory of Gases and Van der Waal's equation.

The chapter on the Phase Rule deserves special comment. Of all the subdivisions of physical chemistry, this has hitherto impressed the student as the least satisfactory. This is not surprising when we consider in what a mist of verbose complexity these comparatively simple matters have generally been shrouded.

Here we have for the first time in English a concise presentation of the fundamental principles which underlie this important contribution, not only to physical chemistry, but to chemistry as a whole; and it is a matter of no little pride to an American that the key to the phase law was furnished by J. Willard Gibbs.

The chapter on Osmotic Pressure and the Gas Law is followed by an Application of the Laws of Gases to Dilute Solutions, and the Freezing-point and Boiling-point methods of determining molecular weights are discussed. Under Electrolytes and Electrolysis there is taken up the method of measuring the Velocity of Ions and the Kohlrausch conductivty method. The chapters on Electrolytic Dissociation, Chemical Dynamics and Statics, Relative Strengths of Acids and Bases, and Applications of the Dissociation Theory, constitute as a whole, perhaps, the most important part of the book.

The work has been very carefully prepared, and Professor Walker has undoubtedly made a valuable contribution to physical chemical literature. The book can be heartily recommended to any student who is just beginning his career in that field which has already revolutionized chemical thought.

HARRY C. JONES.

Leçons de Chimie physique. By J. H. VAN'T HOFF; translated by M. Corvisy. Part II., Chemical Statics. Paris, A. Hermann, 1899. 16×25 cm.; 162 pp.

Under chemical statics the author discusses the "constitution of matters, atoms, molecules, structure and configuration of molecules." We have the atomic theory developed by a man who may, without much exaggeration, be called the founder of modern stereochemistry and modern physical chemistry. The subject is divided into three parts: molecular weight and polymerism; molecular structure and isomerism: molecular arrangement and polymorphism. This arrangement is not only the rational one but the historical one. It is the one we use continually in all our chemical research. When we find two different substances with the same percentage composition, we assume that there is a difference in molecular weight. If this hypothesis be disproved, we try chemical isomerism, stereochemical formulas coming in as a last resort under this head. When this fails, we throw up our hands in despair and classify our ignorance under the caption "physical isomerism."

Under the heading, molecular weight and polymerism, the main subdivisions are: molecular weight determinations in dilute gases, molecular weight determinations in dilute solutions, solid solutions. Under molecular structure and isomerism we have a short section on the determination of constitution and a long one on the determination of configuration. The chapter on physical isomerism deals first with equilibrium relations and then with crystallographic theory. The chief characteristic of physical isomerism as the author uses the term is that it is a function of the solid state only. It is thus a property of the crystal, and for this reason the crystallographic theory finds its place in this chapter.

Apart from the clearness of arrangment and of expression, the book is to be welcomed as a step, possibly an unconscious one, in a new direction. The organic chemistry of to-day, like the inorganic chemistry of to-day, is essentially a qualitative science. We say that one substance loses water or carbonic acid, or something, when treated in a certain way, while another takes up water or hydrobromic acid, or something, when treated in some other way. Further than that we do not go. This state of things will cease so soon as we begin applying the methods and tests of physical chemistry to the problems of organic chemistry. While van't Hoff has sedulously refrained from calling attention to the fair kingdom soon to be overrun by the irrepressible vandals, the physical chemists, he has given us a most excellent map of the outlying country.

WILDER D. BANCROFT.

Scientific Papers, Vol. II. By P. G. TAIT, M.A. Cambridge, The University Press, 1900. Large 4to., cloth, pp. xiv + 500.

The scientific papers of Tait, which are now being published by The University Press, will be completed in a third volume that will contain the final papers of the author, a complete list of all his published articles and a general index. The first volume was considered in the REVIEW for August, 1899. The volume now appearing contains a number of papers on mathematical and physical subjects, among which we enumerate the following: Report on some physical properties of water, 68 pp.; on the foundations of the kinetic theory of gases, 88 pp.; on impact and the path of a rotating spherical projectile, 91 pp.; on the linear vector function, 21 pp.; the articles on thermodynamics, radiation and convection, and quaternions, from the *Encyclopædia Britannica*, 44 pp.; on the teaching of natural philosophy, 15 pp.

Altogether, the volume contains a notable collection of original papers, in which any mathematician or physicist can find much interesting and instructive matter.

We find in this volume that even the play spells of the author have yielded their contribution to science, since the articles on impact and the path of a rotating projectile, arise out of, and are constantly illustrated by, the phenomenal actions of a golf ball. For example, the fact that a golf ball can be "jerked" nearly as far as it can be "driven," seems to have started a long train of reflections in the mind of Tait, and to have resulted in considerable laboratory, as well as field practice. Historical investigation by Tait has also revealed that Newton was familiar with the effects of rotation on a spherical projectile as exhibited by a court tennis ball, and that he gave a theoretical explanation of this effect to which no real improvement or extension had been made up to 1893, when Tait began his papers. Popular articles on the subject by Tait have appeared in *Nature*, and his popular sketch of the main results, so far as they are applicable to the game of golf, will be found in the *Badminton Magazine* for March, 1896.

The subjects of impact, rotation, resistance of the air to moving bodies, and various other phenomena pertaining to the game of golf, are still being pursued by Tait. We must naturally conclude that field practice in the game is a necessary adjunct to these pursuits, if for no other purpose than that of experimental illustration and test of scientific philosophy. The reviewer acknowledges that he has hitherto had a more partial fondness for the erratic curves and twists of a lawn tennis ball, but he has again to acknowledge his indebtedness to Tait for new light upon a subject, and to admit that a desire has been aroused to learn more of the fine points of the game of golf.

ARTHUR S. HATHAWAY.

ROSE POLYTECHNIC INSTITUTE, TERRE HAUTE, IND.

Theory of Screws. By SIR R. S. BALL. Cambridge, The University Press, 1900. 8vo, cloth, pp. xix + 544.

This publication will be welcomed by those who desire to acquire a thorough knowledge of the most recent developments in the dynamics of rigid bodies. Dr. Ball's previous volume on the subject (1876) is not only out of print, but also out of date, on account of the many important additions and extensions that have been since made by him. The present volume, contains the full development of the subject, including the latest, and from a geometrical point of view, the most important piece of work of the author. There is also a set of biographical notes on the principal works that bear upon the subject, a very complete table of contents, and an index. Appendix II. is a reprint of Dr. Ball's exceedingly pointed and humorous address to the mathematical and physical section of the British Association, in 1887, entitled, "A Dynamical Parable." The parable begins, "There was once a rigid body which lay peacefully at rest. A committee of natural philosophers was appointed to make an experimental and rational inquiry into the dynamics of that body." This parable may be regarded as a lively presentation of the trials and difficulties that beset the author in his work on the theory of screws, particularly with reference to the friendly help of the above committee of natural philosophers, Messrs Anharmonic, One-to-One, Helix, Cartesian, Commonsense, and Querulous. It is noted that Mr. Querulous objected at first to serve on the committee because the inquiry was all nonsense, and because anyhow everybody knew as much as they wished to know about the dynamics of a rigid body.

The theory of screws is founded upon the celebrated theorem of Chasles that a rigid body can be moved from one specified position to another by a rotation about a corresponding axis and a translation parallel tot hat axis, and upon the equally celebrated theorem of Poinsot that any system of forces can be replaced by a single force acting along a given axis and a couple about that axis. The motion of Chasles is called a *twist;* the force and couple of Poinsot, a *wrench.* A *screw* is an axis in a definite position with which a definite linear magnitude termed the *pitch* is associated. In a twist about a screw, the pitch is the translation along the axis per unit angle of rotation; in a wrench about a screw, the pitch is the moment of the couple per unit of the force. Thus, when a screw is specified, a twist about that screw has only its amplitude undetermined, and a wrench about it has only the intensity of the force undetermined.

The work of a twist against a wrench on specified screws, the resultants of twists and wrenches, the cylindroid, reciprocal screws, and screw coördinates, constitute the preliminary parts of the subject. The cylindroid is the locus of a screw about which the resultant of variable twists (or wrenches) on two fixed screws, will act. The surface is the locus of a line that meets an axis at right angles and moves up and down in harmonic motion, while turning uniformly round the axis in double the period of the harmonic motion. Such a line traces on a cylinder round the axis the well-known curve that projects into the Lissajou curves of 1 : 2 periods. Reciprocal screws are such that a twist about one does no work against a wrench about the other. The resolution of a twist (or wrench) upon six given screws constitute the coordinates of the twist or wrench referred to the six screws. The coordinates of the screw on which the twist or wrench acts, are the same components to a unit twist or wrench. This coördinate system is a powerful one for the subject, and by taking the six screws of reference mutually reciprocal, the standard interpretations and calculations are made very simple and concise. In fact, one of the striking characteristics of the development is the simplicity and directness with which some of the most important results are obtained. It may be said, briefly, that the theory of screws presents a new set of ideas regarding the motions of a rigid body, which open up a new field for theorems that can only be stated and proven in terms of these new ideas, but which are nevertheless as important in the dynamics of a rigid body as any of the ordinary results.

There is one slip of the author that is unimportant with respect to the subject itself, but which is important as illustrating the dangers of the so-called "infinitesimal" or "indefinitely small" analysis. Ball offers, in Art. 4, p. 8, a geometrical investigation, which proves nothing-unless it be (in accordance with his assumption that the indefinitely small motions of the particles of a body are linear, that there is no indefinitely small motion except a translation. The indefinitely small motions of particles, or of rigid bodies are) in a technical sense, not to be confounded with any actual motions of the body, however small. The term "instantaneous motion" is better, and expresses a motion of the particle or body that could take place under the given conditions, and to which the actual motion of the body will more nearly approximate, the smaller the displacement of the body from its given position. In this language we put before the reader the facts of the case, stated in words that mean what they say, and not in words that must, like "indefinitely small," be considered idiomatically, since taken literally they are either meaningless or express actually an untruth. There are, of course, various "instantaneous motions" according to the character of the motion considered and the degree of approximation sought to the actual motion. In the case of a particle, we have a linear motion along the tangent line, a still better circular motion on the circle of curvature, because it takes into account the changing direction of motion, and highest of all, the motion on the osculating helix of the path. In the case of a rigid body the first approximate motion is only possible when the actual motion is a translation; the second approximate motion, only when the actual motion is a rotation. What Ball is trying to prove is then that in any rigid body moving continuously, the instantaneous motion of each particle in its osculating helix is such that the body would retain its rigidity due to such separate motions of its particles, and be twisting about a definite screw. Algebraically interpreted, the geometric investigation of Art. 4 is an attempt to prove by first differential coefficients and rigidity alone, results that depend upon the second differential coefficients as well as the first. Dr. Ball will find himself in good company in this misapplication of the deceptive infinitesimal analysis, since some of the best mathematicians from Leibnitz down have derived results both true and false by a species of infinitesimal reasoning whose logic was equally infinitesimal in value.

ARTHUR S. HATHAWAY.

ROSE POLYTECHNIC INSTITUTE.

Discourse on the Method of Rightly Conducting the Reason and Seeking Truth in the Sciences. By RENÉ DESCARTES. Translated by JOHN VEITCH. Pp. vi+87. Chicago, The Open Court Publishing Co., 1899.

Elementary Illustrations of the Differential and Integral Calculus. By AUGUSTUS DE MORGAN. Pp. viii+142. Chicago, The Open Court Publishing Co., 1899.

The Evolution of General Ideas. By TH. RIBOT. Translated by FRANCES A. WELBY. Pp. xi+231. Chicago, The Open Court Publishing Co., 1899.

The issuing of these three volumes is in accordance with the educational plan of the publishers to make more generally known the scope and methods of science.

Descartes's *Discourse on Method,* first published in Leyden in 1637, will ever be instructive, and it is particularly appropriate that this essay should be made readily accessible at this day, when so called "scientific method" is so much discussed.

De Morgan's *Calculus* is intended, aside from its interest to mathematicians, to disseminate an adequate appreciation of the methods of the calculus among the public at large. The work originally appeared in 1822, and in the present volume it is reprinted in substantially its original form.

Ribot's *Evolution of General Ideas* is a résumé of psychological lectures given in 1895.

F. B.

Electric Power Transmission, a Practical Treatise for Practical Men. (Second edition.) By LOUIS BELL. New York, Electrical World and Engineer, 1899. Pp. 505.

This new edition of a well-known work differs chiefly from the earlier edition (1897) in the addition of a chapter (XIV.) on the present state of high voltage transmission, the changes in the remainder of the book being of minor importance. As the author points out in his preface, no great advance in power transmission has been made since the issue of the earlier edition, the most important advance being transmission at high voltages and long distances, the highest voltage in commercial use advancing from 14,000 to 40,000, and the distance of transmission from 35 to 80 miles. The paper by C. F. Scott (Transactions American Institute of Electrical Engineers) on high voltage transmission, containing the result of investigations by R. D. Mershon at Telluride, Col., and by other engineers of the Westinghouse Company, is at present our most valuable source of information on this subject and forms an important part of the added chapter. The measurement of the energy losses due to brush discharge between wire and wire through the air is an important contribution to our knowledge. At 20,000 volts this charge is sufficient to be slightly luminous at night and at 50,000 volts the wires are plainly visible for a long distance.

Save for the added chapter, the book is essentially the same as the first edition; it has been the author's purpose to set forth fundamental facts and not to discuss theories of which the practical results are known.

F. Bedell.

The Management of Dynamos. G. W. Lummis. Paterson.

This work is a compendium of information and advice relative to the operation of dynamos and motors. The fundamental physical conceptions of the magnetic field and the generation of an electro-motive force are given in concise form and a complete statement of the behavior of the dynamo, with its faults and their remedy, follows the introductory matter. The arrangement of numbered and lettered paragraphs, especially valuable in a reference work of this class, is to be commended, as is also the fact, that, while the book was written in England it contains nothing that does not bear directly on American practice.

Henry H. Norris.

Ostwald's Klassiker der Exakten Wissenschaften, No. 110. Die Gezetze des chemischen Gleichwichtes für den verdünnten gasförmigen oder gelösten Zustand. By J. H. van't Hoff. Leipzig, Wilhelm Engelmann, 1900. Pp. 105.

No. 110 of Professor Ostwald's reprints contains van't Hoff's well-known paper on the laws of chemical equilibrium, translated by George Bredig. This memoir appeared originally in Swedish and since even for those who read the Scandinavian tongues the Proceedings of the Swedish Royal Academy of Science are not readily accessible, physicists and chemists alike will feel indebted to the translator and to the editor for reproducing it in this available form.

E. L. N.

Volume XII. *February, 1901.* *Number 2.*

THE

PHYSICAL REVIEW.

THE VELOCITY OF IONS DRAWN FROM A FLAME.

By C. D. Child.

A NEW method for determining the velocity of ions in a gas was suggested by Prof. J. J. Thomson in a recent number of the *Philosophical Magazine.*[1] As far as the present writer is aware this has not been used experimentally. It appeared more satisfactory than any method which had previously been used, and an actual test of it seemed desirable. Moreover, it appeared as if a simplification of Professor Thomson's suggestion could be used to advantage in studying the velocity of ions drawn from an electric arc, and it was deemed wise to apply this simplification in the first place to a case that could be made to conform as closely as possible to the theoretical conditions and that could be better tested by comparison with other data. The test was accordingly made by applying the method to the determination of the velocity of ions produced by a flame.

No attempt has been made to secure great accuracy, since the quantity to be measure, *i. e.*, the velocity of the ions, is one depending on a great variety of conditions, and since this work is rather the test of a method than anything else. However, the accuracy of the results here given will compare most favorably with that hitherto secured in attempting to measure such velocities.

The Method Employed.—The method consisted in measuring the potential and the flow of current in a space through which only ions charged with one kind of electricity were passing, and in computing from these measurements the velocity of the ions. It is described by Professor Thomson as follows:

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[1] Phil. Mag. (5), 47, p. 265.

"A very convenient method of determining the velocity of the ions and one which can be applied in nearly every case of conduction through gases, is to produce the ions in one region and measure the electric intensity at two points where there is no production of ions, but to which ions of one sign only can penetrate under the action of the electric field. Thus let A, B, Fig. 1, represent two parallel plates immersed in a gas, and let us suppose that in the layer between A and the plane LM we produce a supply of ions, by any means, and suppose that the gas between LM and B be screened off from the action of the ionizer. Then if A and B are connected to the poles of the battery, a current will pass through the gas, and this current in the region between LM and B will be carried by ions of one sign only. These will be positive if A is the positive pole, negative if it is the negative. Let us find the distribution of electric intensity in the region between LM and B. Let us suppose A is the positive plate. Then all the ions in this region are positive.

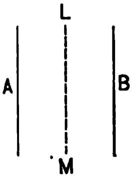

Fig. 1.

Let X be the value of the electric intensity at a point, e the charge carried by each ion, n_1 the number of positive ions, k_1 the velocity of positive ions for unit potential gradient, and x the distance from LM, and we have $\frac{dX}{dx} = 4\pi n_1 e$ and $k_1 n_1 X e = i$ where i is the current through unit area; from these equations we have,

$$X\frac{dX}{dx} = \frac{4\pi i}{k_1} \text{ or } X^2 = \frac{8\pi i}{k_1}x + C^2. \tag{1}$$

Hence if we measure the value of X at two points in the region between LM and B, and also the value of i, we can from this equation, deduce the value of k_1 and hence the velocity of the positive ions in a known electric field. To determine the velocity of the negative ion we have only to perform a similar experiment with the plate A negative."

Objection to Determining the Potential with a Wire.—The more difficult part of the work is to determine accurately the potential.

Two methods have been used for this purpose. A wire has been placed at the point to be investigated, as was done by Zeleny,[1] or a water dropper may be used as in some experiments performed by the present writer.[2] There is the general objection to the use of the wire that it takes a very long time for it to assume the potential of the surrounding space but this is not usually a very serious objection. There is, however, in this particular case a much more serious one.

A body surrounded by a gas can not discharge through the gas, unless there are ions in the gas which are charged with electricity of the opposite sign from that on the body itself. As far as is known ions do not pass from a solid body into gas. They only pass from the gas and give up their charge to the solid. We may perhaps express this idea by saying that the charge can not be driven off from the body. It can only be neutralized by the opposite kind of electricity being attracted to it. Thus in the space *LMB*, Fig. 1, there are only positive ions, if we imagine *A* to be the positive pole. Consequently if a wire which has a negative potential as compared with the surrounding region is placed in this space, it will attract the positive ions and acquire a higher potential. If, on the other hand, it has a positive potential as compared with the surrounding region, it will repel the positive ions and since there are no negative ions to be attracted, it cannot change its potential. As a result of this if there is the slightest unintended leak of positive electricity on to the wire, this electricity will not be able to escape and the wire will register a higher potential than it should.

This unintentional leak of positive electricity on to the wire was especially liable to happen in this case, since the flame producing the ions in the space *LMA* is charged positively, and everything in the room soon became thus charged. It would seem an easy matter to protect the wire from this positive electricity, but in practice it was found difficult to get rid of the last trace of it, and this last trace was entirely sufficient to change the readings. Readings taken with the wire were found to vary from day to day to such an extent that the method was finally abandoned.

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[1] Phil. Mag. (5), 46, p. 47.

[2] Phys. Rev., 6, p. 285.

The idea that the positive charge will not leak off from the wires while a negative one will, is not simply what might be expected from theory. Observation shows the same. If a wire placed in the space *LMB* is charged a few volts lower than the potential of the surrounding space as shown by other methods, it quickly assumed a higher potential. If, on the other hand, it was charged a few volts higher, the change in potential was exceedingly slow and appeared to depend entirely on leakage at other points along the wire rather than on any in the region *LMB*. So clearly was this shown that it afforded a proof of the correctness of the general conception as to how discharge is produced under these condition.

Use of the Water Dropper for Determining Potential.—For this reason the water dropper was used to find the potential in *LMB*. Even with this it was by no means easy to avoid errors due to the charged air of the room. The wires were all placed inside of metal pipes. The switches were placed within a tin box, and were operated by cords passing through small openings. The water dropper itself was entirely surrounded by tin, with the exception of the tube through which the water passed. This was 10 cm. long and 2 mm. in diameter and was placed parallel to the plate B, so that the potential along its whole length was as nearly as possible the same as that at the opening at the bottom. The space between this tube and the metal protecting the water dropper was closed by sealing wax.

The ions from the flame penetrate far more than was to be expected. For a long time it was thought that the water dropper did not register the same potential for different rates of flow, and indeed the writer undertook a series of measurements to show what the relation was between the rate of flow and the potential registered. It was found, however, that enough charged air when carried by the draught from the flame would pass through very small openings to make a difference in the readings of the water dropper, especially when the water was dropping slowly. When at last the water dropper was so insulated that there was no leak onto it, it registered the same potential whatever the rate of flow. This may be offered as proof of the correctness of the determination of potential.

Arrangement of Apparatus.—Fig. 2 gives an outline of the arrangement. A and B are two plates between which the discharge occurs. D is the part of the water dropper between the plates. F is the flame producing the discharge. A and B are connected through the reversing key K to the water battery H. Any point of the battery could be connected to the ground at G. D was connected to the electrometer E.

The distance from the flame to B will be designated by b. This corresponds to the distance in Fig. 1 between LM and B. The difference of potential between the flame and B will be designated by V_b.

The potential of the point D was found by varying H on the battery until the water dropper came to have zero potential. The difference of potential between F and H was then noted. This kept D and its connections at the same potential as the ground, and avoided any error due to leakage from the water dropper.

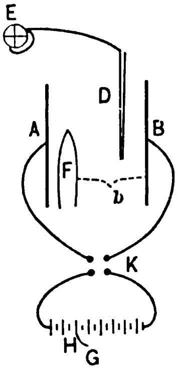

Fig. 2.

The water dropper was placed on a dividing engine so that its position could be easily and accurately changed.

Since the flame F was close to the plate A, it assumed nearly the potential of A and it was found that the potential of F was kept more constant by placing in the flame a wire connected directly to A. Different parts of the flame have, of course, slightly different potentials, but this cause of error could not well be avoided, and in any case the error thus introduced was smaller than other unavoidable errors.

The plates A and B were tin plates 20 cm. in diameter, fastened to boards so as to present to the flame as plane surfaces as possible. The flame was furnished by a row of Bunsen burners 2 cm. apart. These could not be said to ionize a space bounded on one side by an *infinite* plane as LM in Fig. 1, but this arrangement seemed as near an approach to that condition as could well be devised, and apparently satisfied the requirements.

A water battery was used because it was the only means of producing the required potential which the writer had at his command.

It was kept carefully insulated and was found to give practically the same potential on different days. It was calibrated whenever it was used by comparing parts of it at a time with a storage battery and the voltage of the storage battery was measured by a Weston voltmeter.

The electrometer was one designed by Elster and Geitel.[1] For measurents of small potentials it was connected heterostatically and the needle was charged by a water battery. For higher potentials it was connected idiostatically. It was calibrated by comparison with a Weston voltmeter.

Sources of Error.—The observations were rendered inaccurate to a small extent by the movement of the flame and also by the changes in the flame produced by variations in the quality of the gas. Care was taken to keep the flame as constant as possible, and it is believed that these sources of error had but very little effect on the final result.

It was also impossible to determine accurately the boundary between the flame and the surrounding atmosphere, or more correctly between the region where there were ions of both signs and that where there were ions of one sign only. It is not necessary to know where this boundary is in order to use the method as given by Professor Thomson but it is necessary in order to use a modification of it to be described later.

It was found that the gas for about 1 cm. to the right of the visible part of the flame had very nearly the same potential as that of the flame itself, any difference of potential being certainly less than one volt. It is not surprising that this should be so, since the hot air from the lower portions of the flame spreads itself for some distance about the flame proper. This can be easily shown by passing the light from an electric arc through the flame of a Bunsen burner onto a screen behind the burner. The stream of hot air will show itself by the change of refractive index of the air. This region of hot air about the flame was found to coincide practically with that in which the potential was the same as that of the flame.

The method used for finding the boundary between the ionized and unionized regions was to find with the water dropper the point where the potential began to vary from that of the flame. This is not a very satisfactory method, but the only other one possible was to observe the outline of the flame as mentioned above. This later method did not give any more definite results due to the flickering of the flame, and when it was used there remained always the uncertainty as to whether the boundary sought was exactly the same as that shown in the image of the flame on the screen.

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[1] Weid. Ann, 64, p. 680.

Comparison of Potentials with Flame Positively and Negatively Charged.—Table I. gives the result of a set of readings, first when F was charged positively, and second when charged negatively. These are not the average of several sets of readings, but the readings as they were taken down in a single set; b was 8 cm., V_b was 98.5 volts. Column 1 gives the distance from the flame, column 2 the potential in volts below the flame when the flame was charged positively, and column 3 that above the flame when it was negative.

Table I.

1 Distance from Flame.	2 Potential with Flame. +	3 Potential with Flame. −	1 Distance from Flame.	2 Potential with Flame. +	3 Potential with Flame. −
1	2	3	5	49	49
2	13	12	6	64	64
3	23	22	7	81	79
4	36	36			

The differences in the two sets of readings were no greater than are apt to occur in taking two sets with F charged alike in both cases. In fact the results of many trials showed that there was no difference which could be detected with certainty between the form of the curves of potential given when F was positive and that when F was negative. Consequently only the potential taken with F positive are given in the following tables:

Potentials with Different Distances between the Flame and B.—Table II. gives a series of readings taken with different values of b, V_b being in all cases 98.5 volts.

Column 1 gives the distance from the flame. Columns 2, 4 and 6 are observed values of the potential in volts below that of the flame, and columns 3, 5 and 7 are corresponding values computed

TABLE II.

1 Distance from Flame.	2 Observed Potentials.	3 Computed Potentials.	4 Observed Potentials.	5 Computed Potentials.	6 Observed Potentials.	7 Computed Potentials.
1	3	4.4	7	6.7	12	12.3
2	13	12.3	20	19.0	34	34.8
3	23	22.6	36	34.8	64	63.9
4	36	34.8	55	53.6		
5	49	48.7	76	74.9		
6	65	63.9				
7	81	80.6				

by a method to be described later. Columns 2 and 3 are values when b was 8 cm., 4 and 5 when it is 6 cm., and 6 and 7 when it was 4 cm.

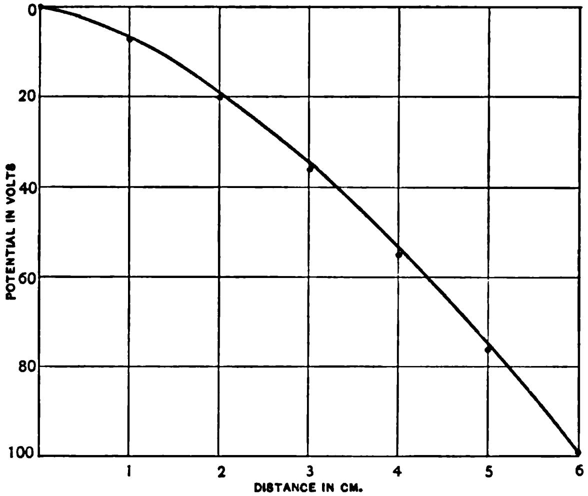

FIG. 3.

The data given in columns 4 and 5 are represented in Fig. 3. The smooth curve represents the theoretical values of the potential, and the points by the side of this line the observed values.

Potential with Different Differences of Potential.—Table III. gives the readings with b always the same, but with different values for V_b, b was 6 cm. Column 1 gives the distance from the flame; columns 2 and 3 the observed and calculated potentials below that of the flame when V_b was 50.5 volts; columns 4 and 5 the potentials for $V_b = 98.5$ volts; columns 6 and 7 for 198.5 volts.

TABLE III.

1 Distance from Flame.	2 Observed Potentials.	3 Computed Potentials.	4 Observed Potentials.	5 Computed Potentials.	6 Observed Potentials.	7 Computed Potentials.
1	4	3.4	7	6.7	16	13.5
2	10	9.7	20	19.0	37	38.2
3	19	17.9	36	34.8	70	70.2
4	28	27.5	55	53.6	108	108.5
5	39	38.4	76	74.9	152	151.0

Determination of Current.—The current between the flame and *b* was found by replacing the plate which had previously been at *B* by one which was 5.6 cm. in diameter, surrounded by a guard ring. The inner diameter of the guard ring was 6.4 cm. and the outer 20 cm. *B* was placed on a dividing engine so that its position could be easily changed.

When the current was large it was measured by a galvanometer, when small, by an electrometer by noting the rate at which a condenser became charged. The capacity of the condenser was found by the use of a ballistic galvanometer. The constant of the galvanometer thus used was computed from its constant when used as a tangent galvanometer. As a check upon this method the capacity was also found from observations of the constant deflection produced in the galvanometer by discharging the condenser through it a given number of times a second. The constant of the galvanometer when used as a tangent galvanometer was found by comparing it with a Weston voltmeter.

The constant of the galvanometer thus used was 4.45×10^{-8} ampère per scale division. The period of the needle was 12.6 sec. making the constant for ballistic work 8.93×10^{-8} coulomb per scale division. The capacity of the condenser was 5.05×10^{-3} microfarad.

The rate of leak of the condenser was small as is shown by the following: The condenser with all of its connections as they were to be used in the determination of the current were charged and the change in potential due to unavoidable leakage noted. This change is shown in Table IV. The leakage is so small that it may be neglected.

TABLE IV.

Time in min.	0	1	2	3	4	5	6
Potential in volts	8.34	7.88	7.62	7.4	7.24	7.06	6.96

Two different sizes of plates were used at B and it was found that the current flowing on to them was proportional to the size of the plates. Whatever variations there were from this rule appeared to be due entirely to errors of observation, so that only one size of plate was used in the measurements here given.

The current was found from the electrometer as follows: B was connected to the electrometer in multiple with the condenser. First it was grounded. The connection to the ground was broken, and after a given length of time the connection to B was broken. The potential of the electrometer was noted and this divided by the length of time equals the rate at which B becomes charged. This was repeated several times and with different lengths of time. The readings taken from time to time gave results which varied but a few per cent. The potentials were found from the readings by the calibration curve of the electrometer. The results from the averages of these readings are given. The change in potential of B was so small when compared with the total difference of potential between B and the flame that it was neglected.

In two cases the values of the currents found by the electrometer were compared with readings found by the galvanometer. When b was 2 cm. and V_b was 98.5 volts and the flame charged positively the deflection of the galvanometer was .15 which was equivalent to 6.55×10^{-9} ampère. The change in potential of the electrometer in 4 sec. was 5.2 volts. The current is equal to the capacity times the voltage divided by the length of time. This gives 6.5×10^{-9} ampère. Similarly the value of the current when the flame was charged negatively as found by the galvanometer was 7.85×10^{-9} ampère and as found by the electrometer 7.4×10^{-9} ampère. It was not possible to be certain concerning the reading of the galvanometer in the last figure. So that the fact that these values so nearly coincide is partly accidental.

Current with Different Distances.—Table V. gives the amount of current flowing with different values for b; V_b in each case being

98.5 volts. Column 1 gives the different distances. Column 2 the current when the flame was positive and 4 when it was negative. It may be noticed that the current varies approximately inversely as the cube of the distance. Columns 3 and 5 give the values calculated on this assumption assuming also that the values given in the table for 2 cm. are correct. The theoretical reason for this law will be discussed later. These values are not for *i* as given in the formulæ, but for the total current flowing on to the plate 5.6 cm. in diameter.

TABLE V.

1 b	2 Observed Current with Flame. +	3 Computed Current with Flame. +	4 Observed Current with Flame. —	5 Computed Current with Flame. —
1	$652. \times 10^{-10}$	$521. \times 10^{-10}$	$1065. \times 10^{-10}$	$610. \times 10^{-10}$
2	65.2 "	65.2 "	76.2 "	76.2 "
3	7.9 "	8.15 "	9.3 "	9.5 "
4	2.12 "	2.41 "	2.43 "	2.82 "
5	.65 "	1.02 "	.91 "	1.19 "

The current for 1 cm. was measured with the galvanometer, for 2 cm. with both the galvanometer and the electrometer, the average values being given. The currents for the other distances were determined with the electrometer.

Current with Different Differences of Potential.—Table VI. gives the amount of current for different values of V_b, b in each case being 6 cm. Column 1 gives V_b, column 2 the current when the flame is positive, column 3 when it is negative. In this case the current varies nearly as V_b^2. Columns 3 and 5 are computed on this assumption.

TABLE VI.

1 V_b	2 Observed Current with Flame. +	3 Computed Current with Flame. +	4 Observed Current with Flame. —	5 Computed Current with Flame. —
50.5	$.50 \times 10^{-10}$	$.51 \times 10^{-10}$	$.52 \times 10^{-10}$	$.58 \times 10^{-10}$
98.5	2.12 "	2.12 "	2.43 "	2.43 "
198.5	8.8 "	8.6 "	9.05 "	9.25 "

This law seemed important enough to test again, especially since the deflection in the electrometer was here so small that an error in the last figure of the reading would produce a large percentage of error. A similar set of readings was accordingly taken with b equal to 4 cm. These readings and the computed values are given in Table VII.

TABLE VII.

1 V_b	2 Observed Current with Flame. +	3 Computed Current with Flame. +	4 Observed Current with Flame. —	5 Computed Current with Flame. —
50.5	1.87×10^{-10}	1.9×10^{-10}	2.5×10^{-10}	2.48×10^{-10}
98.5	7.9 "	7.9 "	10.3 "	10.3 "
198.5	32. "	30. "	40.3 "	39. "

All of these readings in the last two tables were taken with the electrometer.

Calculation of k.—If in equation (1) we let x_1 and x_2 be two particular values of x, and X_1 and X_2 corresponding values of X, we have

$$X_2^2 - X_1^2 = \frac{8\pi i}{k_1}(x_2 - x_1)$$

or

$$k_1 = \frac{8\pi i(x_2 - x_1)}{X_2^2 - X_1^2}.$$

This equation is expressed in the electrostatic system. The values given in the tables are given in the practical system. The above equation when expressed in this system becomes

$$300k_1 = \frac{8\pi i \times 3 \times 10^9(x_2 - x_1)}{(\frac{1}{300})^2(X_2^2 - X_1^2)}$$

or

$$k_1 = \frac{72\pi i \times 10^{11}(x_2 - x_1)}{X_2^2 - X_1^2}. \qquad (2)$$

If we take the case when the total distance b is 6 cm. and V_b is 98.5 volts, if x_1 and x_2 are equal to 1 and 5 respectively we find from Fig. 3 that $X_1 = 9.8$ and $X_2 = 22$. To find the current per unit cross-section the currents given in Table V. must be divided by the area of the plate B. This was $2.8^2\pi$. This gives the value for i in this case to be $.89 \times 10^{-11}$. Substituting these values in (2) we have $k_1 = 2.08$ cm. per second for a volt per cm.

Wilson[1] found the velocity of the positive ions in the flame itself to be in some cases as high as 50 cm. per second, and that of the negative 1000 cm. per second. McClellan[2] found the velocity of the positive ions in the hot air above the flame to vary from .22 cm. to .03 cm. per second.

It is evident that in finding X_1 and X_2 graphically we are liable to introduce an error due to a wrong estimate of the tangent to the curve. This is more serious since the denominator of the fraction in (2) is the difference between the squares of two quantities each liable to such an error. Moreover, it seemed to be impossible to find the potential at any point nearer than one volt, and an error of one volt in the potential affected the tangent to the curve quite materially. It was estimated that it would be quite possible for an error of ten per cent. due to this cause to occur.

Simplification of the Method.—There is, however, another way in which k_1 can be computed which will now be considered. It is seen that the potential gradient in Fig. 3 at the flame is quite small. The explanation of this appears to be as follows: The number of ions in the flame is exceedingly large compared with the number actually drawn toward B. When this is the case the amount of discharge is not limited by the number of ions in the flame, but by the change in potential in LMB produced by the ions there.

We may show this mathematically as follows: If V equals the potential at any point in LMB and $a = \frac{8\pi i}{k_1}$, we may write equation (1)

$$\frac{dV}{dx} = -\sqrt{ax + C^2}$$

where C is the value of $\frac{dV}{dx}$ at the origin. The negative sign before the radical corresponds to the case imagined, the plate B being negative, the flame positive. Integrating this equation we have

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[1] Proc. Roy. Soc., '1899.

[2] Phil. Mag., 46, 41.

$$V = -\frac{2}{3a}\left\{(ax + C^2)^{3/2} - C^3\right\} \qquad (3)$$

if $V = 0$ at the origin.

If we place the origin at the edge of the flame, *i. e.*, at LM in Fig. 1, C is nearly equal to zero as is shown graphically in Fig. 3. This may also be shown from theoretical considerations. If N_1 is the number of positive ions at LM equation $k_1 n_1 X\varepsilon = i$ becomes $k_1 N_1 C\varepsilon = i$. If we substitute this value for i in equation (3) we get an equation of the fourth degree in C. We can not solve this algebraically, but we can get an approximate value if we assume C to be small, and the experimental work has shown that this is a safe assumption to make. Substituting this value for i in equation (3), making this assumption, remembering the $a = \frac{8\pi i}{k_1}$ and that if C is small, N_1 must be large, we find as an approximation that

$$C = \frac{9V^2}{32\pi x^3 N_1\varepsilon}.$$

We can get some idea of the value of $N_1\varepsilon$ from the work which has been done on the conductivity of flames. Thus in the flame $i = N_1\varepsilon X(k_1 + k_2) = \frac{X}{\rho}$, if we assume the number of positive and negative ions to be the same, and if ρ is the resistance of a cube 1 cm. on each side. Or $N_1\varepsilon = \frac{1}{\rho(k_1 + k_2)}$. Data is given by Marx[1] from which a value for ρ for an ordinary Bunsen burner flame may be computed. From his data we find that we will not be far wrong to assume $\rho = 3 \times 10^6$ ohms or $\frac{1}{3} \times 10^{-5}$ E. S. unit. It will also be safe to say that $(k_1 + k_2)$ in E. S. units is not greater than 3×10^5 which gives 1 for the value of $N_1\varepsilon$.

If $V_b = 100$ volts when $b = 6$ cm., we have $C = 4.6 \times 10^{-5}$. The value for a in the same case and in the same units is 1.16×10^{-3}. The ratio of C^2 to ax when $x = 1$ is 1.83×10^{-6}, that is, any error which would be caused by dropping C would be less than .0002 per cent. when $x = 1$ cm., and would be still smaller as x becomes greater.

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[1] Drude Ann., 2, p. 787.

All of this is, of course, only a rough approximation, but it will serve to show that in the case of discharge from a flame C is so small that we may safely neglect it in equation (3).

If we place $C = 0$, equation (3) becomes

$$V = -\tfrac{2}{3} a^{\frac{1}{2}} x^{\frac{3}{2}} \tag{4}$$

If we plot this giving to a such a value that $V = 98.5$ volts when $x = 6$ cm., we will have the smooth curve drawn in Fig. 3. The points which were found from observation were all near to the curve. Values of V computed in this same way are given in columns 3, 5 and 7, Table II. and columns 3, 5 and 7, Table III.

In all these cases there are no great differences between the observed and the calculated values. We therefore consider ourselves justified in supposing that in these cases the value of $\frac{dV}{dx}$ at the origin is practically zero. Substituting the value of a in equation (5) and solving for i we have $i = \frac{9V^2k_1}{32\pi x^3} = \frac{9{V_b}^2k_1}{32\pi b^3}$ when $x = b$. This gives a theoretical basis for the fact already noticed that the current varies approximately as $\frac{V_b^2}{b_3}$. The deviations from this rule will be discussed shortly.

If we have an unlimited supply of ions in the flame so that equation (4) holds good, and if we can measure V_b together with i, we can compute k_1 without measuring the potential in the space LMB. We thus do away with the error arising from mistaking the tangents to curve on Fig. 3. However, we introduce another source of error in most cases, due to the difficulty of determining the boundary LM. But in the case of the flame when the distance b is 4 cm. or more, this error is at least not greater than the other, and the latter method of computing k_1 is very much simpler.

If we express the quantities in the practical system the above equation becomes

$$k_1 = \frac{32\pi i \times 10^{11} b^3}{V_b^2}.$$

Table VIII. gives a series of values for k_1 and k_2, the velocity of positive ions for unit potential gradient, which have been computed by this formula from Table V. where V_b is 98.5 volts.

TABLE VIII.

1 b	2 Current with Flame. +	3 Current with Flame. —	4 k_1	5 k_2	6 k_2/k_1
1	275 × 10⁻¹¹	450 × 10⁻¹¹	2.85	4.66	1.64
2	27.5 "	32.1 "	2.27	2.65	1.17
4	13.34 "	3.92 "	2.21	2.60	1.18
6	.893 "	1.08 "	2.00	2.41	1.20
8	.274 "	.384 "	1.45	2.03	1.40

Column 1 gives the distance b; column 2 the current for unit area when the flame was positive; column 3 when it was negative. Columns 4 and 5 give corresponding values for k_1 and k_2. Column 6 gives the ratio between these values.

Variation of k.—We see here a very decided tendency for the values of k_1 and k_2 to become smaller as the distance becomes greater. Two explanations for this may be suggested. One is that the ions move more slowly the longer the time that elapses after they leave the flame. The other is that the apparent change in velocity is due to errors of measurement, that the large values at first are due to an error in the estimate of the position of the boundary about the flame, and that the smallness of the current when the distance was 8 cm. was due to the fact that with increase of distance between the flame and B the finite size of the plates and flame comes to produce a very large error.

Let us consider the time that actually elapses during the passage of the positive ions from the flame to B, assuming that k_1 is constant and that $V = -\frac{2}{3}a^{\frac{1}{2}}x^{\frac{3}{2}}$. Let T_1 equal this length of time.

$$T_1 = \int_0^{T_1} dt = \int_0^b \frac{dx}{k_1 \dfrac{dV}{dx}} = -\int_0^b \frac{dx}{k_1 a^{\frac{1}{2}} x^{\frac{1}{2}}} = -\frac{1}{2}\,\frac{b^{\frac{1}{2}}}{k_1 a^{\frac{1}{2}}} = \frac{b^2}{3k_1 V_b}.$$

Similarly T_2, the time that it takes for the negative ions to pass from the flame to B, equals $\dfrac{b^2}{3k_2 V_b}$. This will also be correct when we express the quantities in the practical system. For example, if $b = 4$ cm., $V_b = 98.5$ and $k_1 = 2.26$ cm. per sec. per volt, $T = .024$ sec.

We see that the time becomes great when b is increased and also when V_b is diminished, and changing the values of V_b does not introduce any of the possible errors which have been suggested as causing the changes in the values of k_1 and k_2.

Accordingly the values of k_1 and k_2 when V_b varies are given in Table IX. These values are computed from the data of Tables VI and VII.

TABLE IX.

1 V_b	2 Current with Flame. +	3 Current with Flame. —	4 k_1	5 k_2
50.5	$.21 \times 10^{-11}$	$.232 \times 10^{-11}$	1.78	1.86
98.5	.893 "	1.08 "	2.00	2.41
198.5	3.7 "	4.04 "	2.04	2.23
50.5	$.787 \times 10^{-11}$	$.945 \times 10^{-11}$	1.92	2.39
98.5	3.34 "	3.92 "	2.21	2.60
198.5	13.5 "	16.5 "	2.2	2.76

Column 1 gives the values of V_b. The other columns given are the same as in Table VIII. The first three values for k_1 and k_2 are derived from Table VI where b was 6 cm.; the last three from Table VII where b was 4 cm.

We see that there appears to be a slight decrease in k_1 and k_2 as the differences of potential become smaller. The time varies inversely as the *first* power of V_b but directly as the *square* of b, so that we have a variation in T_1 by changing b from 1 cm. to 8 cm. which is sixteen times greater than that secured by changing V_b from 50.5 to 198.5 volts. Table IX is at least in harmony with the idea that k_1 and k_2 decrease as T_1 and T_2 increase.

If there were any great variation in k_1 it would show itself in the curve in Fig. 3. Thus if k_1 instead of being a constant decreases as T_1 increases, the values for the potential would be somewhat higher than they are. For instance if $k_1 = k_1'\left(1 - \frac{t}{15}\right)$ where k_1' is a constant the values for V which we would have in Fig. 3 when $x = 4$ cm. would be 55.9 instead of 53.6. In fact the values of the potentials in Tables III., IV., and V. are slightly larger than the theoretical values. While this by itself would mean little we can say that this also is in harmony with the other data.

What is more decisive than anything else, is that we know from the work of others that the velocity of ions in the flame is very much greater than that of the ions in the hot air above the flame, and consequently a change must take place at just the region which is being investigated. The writer is, therefore, of the opinion that the change in velocity as b is moved from 1 cm. to 6 cm. is largely a real change, but that the change in going from 6 cm. to 8 cm. is due rather to lack of conformity between the actual and ideal conditions, since there does not seem to be any reason why so large a change should occur at that place.

If this conclusion is correct none of the equations which have been given are strictly true, for it was tacitly assumed that k_1 was a constant. No doubt k_1 always varies more or less and the equations are to a certain extent incorrect, but they at least give a close approximation, and it is not probable that k_1 would often vary as rapidly as it does in this case.

Simplification Applied Qualitatively.—The simplification here suggested will also enable one to tell something about the *relative* velocities of the positive and negative ions in cases which can not be considered analytically. In order to determine this relative quantity in the case just considered it was only necessary to compare the rate of discharge when B was positive with that when B was negative. In fact that is all that is necessary in any case of discharge from a place where there is an unlimited supply of ions of both kinds, whether the surfaces are of such a shape that they can be treated analytically or not.

Let us consider the case where LM and B in Fig. 1 are surfaces of any shape. If we imagine the current to be in the beginning zero, as it increases the number of positive ions in LMB increases, the potential in this region increases, and the fall of potential at LM decreases until finally the fall of potential at LM is so small that only a sufficient number of ions are drawn past LM to maintain the current.

The current would not be limited by the number of ions in the flame, but it would be choked, due to the number of ions present in the LMB. And this number would be greater for a given current the slower the movement of the ions. If under similar conditions the current is greater with positive ions in LMB than with negative ones, it shows that the velocity of the positive is the greater, and vice versa.

This holds where LM is a plane, a cylinder as with a single Bunsen burner, or a sphere as with an arc. It holds whether LM is a regular surface or not. The modification of the mathematical work to the cases of the cylinder and the sphere is entirely feasible in case it may be desired.

Comparison of this Method with Other Methods.—The disadvantages of this method have been apparent in the preceding description. If one uses the method as first given by Professor Thomson, there must ever be more or less uncertainty in determining the tangent to the curve of potentials, and this error would become more serious as the supply of ions in ALM becomes smaller. For then the fall of potential in LMB would become more nearly uniform, X_1 and X_2 would be nearly the same, and any error in either would produce a much larger error in the difference of their squares.

The modification suggested here is generally liable to error due to uncertainty as to where LM is, and moreover it cannot be used at all when the source of ions in LMB is small. The greatest source of error in the preceding work, *i. e.*, changes in the position and character of the flame is not one which is in any way due to the method used.

Summary.—We may summarize the preceding paper as follows:

First, an application of the method suggested by Professor Thomson shows that the velocity of the positive ions drawn from a Bunsen burner is approximately 2.2 cm. per sec. for potential gradient of one volt per cm., and that for negative ions 2.6 cm.

Second, in the case of an unlimited supply of ions, if the discharge takes place between two regular surfaces the velocity may be determined by simply measuring the current per unit area and the difference of potential between these surfaces, and if the surfaces are not at all regular, the relative velocities of the positive and negative ions may be determined by comparing the positive and negative currents.

A description will be given in another article of an application of this simplified method to the comparison of the velocities of the positive and negative ions drawn out from an electric arc.

Colgate University, Nov. 21, 1900.

THE EXACT RELATION BETWEEN OSMOTIC PRESSURE AND VAPOR PRESSURE.

By Arthur A. Noyes.

1. Introduction.

THE earlier thermodynamical derivations of the relation between osmotic pressure and vapor-pressure were inexact, inasmuch as the influence of the compression of the liquid was neglected. From the failure to take this influence into account, has resulted in my opinion an erroneous conception of the volume-factor by which the osmotic work must be divided in order to give the osmotic pressure. Two years ago, Abbot and myself[1] published a derivation based on the consideration of an osmotic column which appeared to be free from these imperfections. In a later publication[2] I still further discussed the above-mentioned volume-factor. Dieterici[3] in a recent article, has, however, raised certain objections to my views, and to the derivation of the relation by means of the osmotic column. His remarks, so far as they are of a personal nature, need not be considered. It would also be unprofitable for me to enter into an immediate discussion of the scientific considerations in Dieterici's article. In order to make the matter entirely clear, it seems, instead, necessary to deduce anew the relation in question, taking into account the relatively small factors which are involved. Incidentally, I will discuss those remarks and objections of Dieterici which seem to be of importance.

2. Definition of Osmotic Pressure.

Before deriving the relation between vapor-pressure and osmotic pressure, it is necessary to have a clear and precise conception of the latter property. We define osmotic pressure to be the pressure exerted on a semipermeable wall which separates a solution from its solvent. In order that the two may be in equilibrium with each other and no passage of solvent through the semipermeable wall take place, it is necessary that the solution be subjected to a greater external pressure than the solvent; the difference in the two external pressures is then equal to the osmotic pressure, and a measure of it. It is to be noted that this pressure-difference, or the osmotic pressure of the solution, will, like vapor-pressure, vary with the absolute value of the external pressure or with the degree of compression of the solution, as well as with the temperature.

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[1] This Review, 5, 113.

[2] Die Beziehung zwischen osmotischer Arbeit und osmotischem Druck, Ztschr. für physik. Chem., 28, 220.

[3] Ztschr. für physik. Chem., 29, 139.

To make this definition clearer, consider two special cases which will be of importance in the subsequent considerations. In the figure, let A be a solution and B a solvent separated from each other by a fixed semipermeable wall EE, and enclosed by pistons C and D on which any desired pressure can be exerted. First, suppose that the pressureon piston D is made equal to the vapor-pressure p_0 of the solvent. Then to produce equilibrium, a pressure of $P_1' + p_0$ must be exerted on piston C, where P_1' is the osmotic pressure exerted on the wall E by the *compressed* solution. It is to be noted that the vapor-pressure of the solution has been increasea by the compression from its normal value p_1 to p_0, that of the solvent, this being required by the Second Law, since a system which at constant temperature is in equilibrium in one way must be in equilibrium in every way.

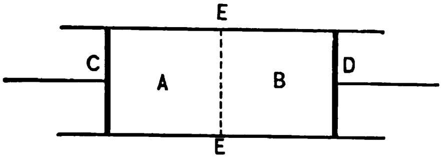

Fig. 1.

Second, suppose that the pressure on piston C is made equal to the vapor pressure p_1 of the solution. Then equilibrium may be brought about by producing on piston D a pressure of $p_1 - P_1$ where P_1 is the osmotic pressure of the solution when standing under its vapor pressure p_1. The vapor pressure of the solvent is reduced by its expansion to that (p_1) of the solution, for the reason before stated.

It is necessary to add that the above definition does not fully coincide with that usually given, osmotic pressure being ordinarily defined as the total difference in pressure between a solution and solvent separated by a semipermeable wall when each stands under only its own normal vapor-pressure. This total pressure difference (π_1) is evidently the sum of the true osmotic pressure (P_1), as above defined, and the difference in vapor-pressures (p_0 and p_1) of the solvent and solution. That is, $\pi_1 = P_1 + p_0 - p_1$. The quantity π_1 is, however, a pressure that does not correspond to a condition of equilibrium, and could therefore never be directly involved in a reversible process. It is, moreover, the sum of two independent kinds of pressure which vary according to different laws with the temperature and volume, and are differently related to each other in the case of different solvents. Its use seems, therefore, from a physical standpoint, very inadvisable.

3. JUSTIFICATION FOR THE EMPLOYMENT OF LIQUIDS WITH NEGATIVE PRESSURES.

If, as is ordinarily the case, the osmotic pressure of the solution be greater than the vapor-pressure, it would be necessary in the second arrangement for equilibrium described above to subject the solvent to a negative pressure, which in the case of concentrated solutions would have a very high value. It has not, however, hitherto been found practicable even under the most favorable conditions, to make liquids withstand, without breaking apart, a negative pressure much exceeding one atmosphere. On this ground Dieterici has denied the validity of the relation between osmotic pressure and vapor-pressure derived by Noyes and Abbot, for the osmotic column considered by them stands under a negative hydrostatic pressure, and he insists in the words of Nernst that a process or equilibrium-condition to which the Second Law is applied must be "wenigstens prinzipiell experimentell realizirbar." It will be readily seen, however, that this requirement is in reality fulfilled, for though high negative pressures are unattainable, yet, since small ones have been realized, it is always possible to devise a process or arrangement involving the summation of these small pressures, so that the same final result is produced as if the large negative pressure were directly applied. Thus, if one gram of a solvent is to be removed from a solution so concentrated that the requisite negative pressure on the solvent cannot be realized, a series of solutions of gradually decreasing concentration might be employed for the purpose, each one taking up the gram of solvent from one a little more concentrated and giving it off to one a little more dilute, these intermediate solutions thus undergoing no permanent change and the results being the same as if the solvent were withdrawn directly. Similarly, if the solution is so concentrated that a column of solvent of the height necessary to compensate the osmotic pressure will not hold together, a column of the same height can be built up in sections, provided with semipermeable walls at their tops, and filled with a series of solutions of varying concentrations, increasing as one passes upwards; since such a column is in equilibrium at its top with the concentrated solution and at its bottom with pure solvent standing under its vapor-pressure, its pressure relations must be the same as that of a column of solvent which at its two ends is in equilibrium with the same pressures.

Although the employment of negative pressures is thus justified even in accordance with the assumed requirement that the conditions must be "wenigstens prinzipiell experimentell realizirbar," I feel it is important to add a few words in regard to this dictum, which as interpreted by Dieterici, leads to the absurd result that the thermodynamic relation between osmotic and vapor pressure derived by Noyes and Abbot is exact as long as the osmotic pressure does not exceed the negative pressures which liquids have thus far been found to sustain, but ceases to be valid for slightly higher pressures. The following seems to me a more correct as well as a more definite statement of the matter. What is essential in order that the application of the quantitative form of the Second Law may lead to useful results is the knowledge first of the nature of the intensity-factor within the system which must be compensated in order that the change in question may take place reversibly, and secondly, the knowledge in each special case, of the relation of this intensity-factor to the work involving it, since it is always two quantities of *work* which are brought into relation to each other by the application of the Second Law to an isothermal cyclical process. If these facts in regard to the intensity-factor are known, it is a matter of indifference what external mechanical or other device be employed for its compensation, or whether any such device has been experimentally realized or even imagined. In order that this knowledge in regard to the intensity-factor may rest on a firm experimental basis, it is necessary, to be sure, that some device for its measurement shall have been realized, and that reliable measurements of it shall have been made.

Briefly expressed, the points which I desire to emphasize are that the quantitative form of the Second Law is applicable to every reversible change whether experimentally realizable or not, and that any uncertainty that may attach to the conclusions drawn from it in regard to the intensity-factor involved in the change, arises not from the fact that the Second Law is not applicable to ideal changes, but because the nature of the intensity-factor to be compensated and the form of the condition equation containing it, may not have been correctly understood. For example, van't Hoff's original deduction of the relations of osmotic pressure to vapor-pressure or to freezing-point-lowering is correct, provided his conception of osmotic pressure as the intensity-factor whose external compensation will make the process of addition or separation of the solvent reversible, and his assumption in regard to the volume factor involved, are correct; the validity of his deduction is, however, independent of the experimental realization or mental conception of devices like semipermeable walls which may serve for the compensation of the pressure, except in so far as such devices may actually have been used to demonstrate experimentally the correctness of the conception of osmotic pressure and of its assumed relation to the calculated osmotic work.[1] It should not be forgotten, however, that this requisite knowledge can often be also obtained in an indirect or theoretical manner; and that the degree of certainty which often attaches to it, though not complete, may still be very great. It may, moreover, be pointed out that the certainty of the conclusions drawn from the cyclical process is not greatly increased by a mere qualitative demonstration of the realizability.

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[1] Two further illustrations of the matter under consideration may be taken from Nernst's Theoretische Chemie, 2d edition, pp. 101 and 226. The first case involves the calculation of the work obtainable by the reversible mixing of two different gases, and the author insists that the validitity of the thermo-dynamic relation derived is dependent upon the actual realization of suitable semipermeable walls. In my opinion, however, its validity rests solely on the correctness of the assumption that the partial pressure of each of the two gases in the mixture is the same as if each gas were present alone, an assumption which, to be sure, can be directly tested only through the realization of the

4. Derivation of the Relation by Means of a Cyclical Process.

Consider a cyclical process carried out at constant temperature with the apparatus shown in Fig. 2, in which *A* is a solution of osmotic pressure P_1 and vapor pressure p_1 separated from the pure solvent *B* by a semipermeable wall *EE* and in contact with vapor of the solvent in the space *F* at the pressure p_1. By means of piston *D* a pressure $p_1 - P_1$ is exerted on the solvent *B* just sufficient to prevent it from entering the solution.

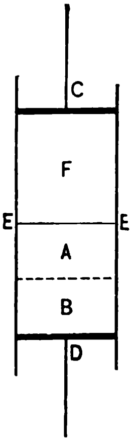

Fig. 2.

Start with one gram of solvent-vapor in the space *F* and an indefinite small quantity of liquid solvent under the piston *D*, and carry out the following isothermal process:

1. Slightly increase the pressure on piston *C* until one gram of the vapor (of volume v_1 at pressure p_1) condenses into the solution and passes out through the wall *EE* (occupying the volume V' at the pressure $p_1 - P_1$). In this process the solution undergoes no permanent change.

2. Close the openings of the wall *EE* and allow the one gram of liquid solvent just obtained to contract until the pressure becomes equal to its normal vapor-pressure p_0 and the volume becomes V_0.

3. Reduce slightly the pressure p_0 on the piston until the gram of solvent vaporizes, forming the volume v_0 of vapor at the pressure p_0.

semipermeable walls. The second example concerns the relation between the amounts of work involved in passing isothermally from the liquid to the gaseous condition, in one case at constant vapor pressure, and in the other case along the pressure volume curve predicted by van der Waal's equation. The author does not regard the conclusion reached absolutely binding, for since the realization of the second operation is impossible, he considers that the application to it of the Second Law is questionable. It seems to me, however, that the conclusion is uncertain only to the extent to which the validity of van der Waal's equation is uncertain.

4. Allow the vapor to expand until its pressure becomes p_1 and its volume v_1. The cyclical process is now complete.

The amounts of work W done by the system in the four parts of the process are:

$$W_I = -p_1v_1 + (p_1 - P_1)V'$$

$$W_{II} = \int_{V'}^{V_0} PdV$$

$$W_{III} = p_0v_0 - p_0V_0$$

$$W_{IV} = \int_{v_0}^{v_1} pdv$$

But by the Second Law

$$W_I + W_{II} + W_{III} + W_{IV} = 0,$$

or

$$\int_{v_0}^{v_1} pdv + p_0v_0 - p_1v_1 = -\left(\int_{V'}^{V_0} PdV + (p_1 - P_1)V' - p_0V_0\right)$$

Now since in general:

$$p_bv_b - p_av_a = \int_{v_a}^{b} pdv + \int_{p_a}^{p_b} vdp$$

it follows that:

$$\int_{p_1}^{p_0} vdp = \int_{(p-P_1)}^{p} VdP. \tag{2}$$

Equation (2) is the most general and an absolutely exact expression of the relation between vapor pressure and osmotic pressure.

If in the case of the solvent, as is always approximately the case for moderate pressures, the decrease in volume is proportional to the increase of pressure, that is, if

$$-\frac{V - V_0}{V_0} = k_0(P - p_0) \text{ or } V = V_0 - V_0k_0(P - p_0) \tag{3}$$

where k_0, the compression-coefficient of the solvent, is constant, then the second member of (2) can be integrated.

$$\int_{p_1-P_1}^{p_0} VdP = (V_0 + V_0k_0p_0)\int_{p_1-P_1}^{p_0} dP - \frac{V_0k_0}{2}\int_{p_1-P_1}^{p_0} 2PdP$$

whence follows:

$$\int_{p_1}^{p_0} v\,dp = (P_1 + p_0 - p_1)V_0\left(1 + \frac{(P_1 + p_0 - p_1)k_0}{2}\right) \qquad (4)$$

This expression can be simplified in form, but not in significance, by substituting for $(P_1 + p_0 - p_1)$ the total pressure-difference π_1. (See above.) It then becomes:

$$\int_{p_1}^{p_0} v\,dp = \pi_1 V_0(1 + \tfrac{1}{2}\pi_1 k_0) \qquad (5)$$

5. Derivation of the Relation by Consideration of the Equilibrium of an Osmotic Column.

This same relation can be derived still more simply by a consideration of the conditions of equilibrium which must prevail in an osmotic column. This was attempted in the earlier article by Noyes and Abbot, but as Dieterici has called attention to an error in the sign of the compression term of the formula derived, and as the deduction can be given much more briefly and clearly than was done at that time, I may be permitted to present the matter anew. A vertical tube which is provided[1] with a fixed semipermeable wall near its top opens below into an open vessel. Above the wall is placed an infinitely thin layer of any solution, and the tube and the vessel below it are filled with the pure solvent. The whole is enclosed within a space containing only the vapor of the solvent. Equilibrium would be established by the passage of a small quantity of the solvent through the wall into or out of the solution. If p_1 is the vapor-pressure and P_1 the osmotic pressure of the solution, the solvent just below the wall must then be under the pressure $p_1 - P_1$, in order to compensate the opposite pressures of the solution. On the other hand, the vapor from the solution must be in equilibrium with that from the solvent at the semipermeable wall that is, both must have the same pressure p_1, since otherwise perpetual motion of the second kind would be possible. The pressure on the solvent at its surface in the vessel is, however, its vapor-pressure p_0, and it is evidently possible by the general law of statical pressure to determine, on the one hand the height above the surface at which the pressure of the vapor would become p_1, and on the other that at which the pressure of the liquid column of solvent would become $p_1 - P_1$. Since these two heights must be equal, a relation between osmotic and vapor pressures is thereby obtained. Namely, since the difference in pressure at any two heights is equal to the weight of the intervening column of vapor or liquid solvent, we have the relations

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[1] For a figure illustrating the arrangement, see PHYSICAL REVIEW, 5, 114.

$$\delta dh = -dp \text{ and } \Delta dh = -dP$$

where δ and Δ are the densities of the vapor and liquid respectively, and dp and dP are their respective changes in pressure; or:

$$dh = -vdp \text{ and } dh = -VdP$$

where v and V are the (variable) specific volumes of the two. If the height of the wall above the surface is h_1, we have

$$\int_0^{h_1} dh = h_1 = -\int_{p_0}^{p_1} vdp = -\int_{p_0}^{p_1 - P_1} VdP$$

which is a relation identical with equation (2) derived by the cyclical process. From it, by substitution of the compression-coefficient (see equation (3)) equations (4) and (5) are obtained as before.

6. DISCUSSION OF THE DERIVED RELATION.

These equations contain, as Dieterici points out, a quantity which can not be directly experimentally determined, namely k_0, which is the mean compression-coefficient of the solvent between the pressures p_0 and $p_1 - P_1$, the latter of which is in general negative. This is true, and the fact does introduce, it must be admitted, a certain degree of uncertainty into practical applications of the formula: when it is considered, however, that the measurements of various investigators have shown that the compression-coefficient varies but slightly even for considerable variations of positive pressures,[1] it seems highly probable that the value for moderate negative pressures will not be greatly different from that for low positive pressures. Moreover, the error in the compression coefficient would have to be very large indeed, in order to produce an appreciable effect upon the calculated value of the osmotic pressure; for the whole term $\frac{1}{2}\pi k_0$ has a relatively small value, even for quite concentrated solutions; thus an ether solution must have an osmotic pressure of about 120 atmospheres, an alcohol solution one of 250 atmospheres, and a water solution one of 400 atmospheres, before this term amounts to one per cent.

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[1] Compare the summary of values in Landolt and Börnstein's Tabellen, p. 265. One or two examples may be here cited: alcohol at 28° has a coefficient of 86×10^{-6} between 150 and 200 atmospheres, and of 81×10^{-6} between 150 and 400 atmospheres; for ether at 13° the value is 168×10^{-6} between 8.4 and 13.9 atmospheres, and 165 between 8.4 and 36.5 atmospheres.

It is to be especially pointed out that the volume-factor which occurs in the above equations is the volume of one gram of the *solvent* under its normal vapor pressure corrected by a term (relatively small even for fairly concentrated solutions) representing the effect of its compression. But the factor which has hitherto been used by Dieterici and others in calculating the osmotic pressure from the integral $\int_{p_0}^{p_0} pdv$ is the *change in the volume of the solution* that occurs when one gram of solvent is added to an indefinitely large quantity of the solution. These two volume-factors have, however, essentially different values in the case of even moderately concentrated solutions, as is shown by the following table which contains the results for sulphuric acid solutions.[1] The first column contains the concentration in mols per liter; the second, the value of the integral $\int_{p_1}^{p_0} vdp$ at 0°, as determined experimentally by Dieterici, this being approximately equal to the osmotic pressure in kilograms per square centimeter; the third, the volume change V_1, when one gram of water is added to an infinite amount of the solutions, as calculated by Dieterici; the fourth, the value of $V_0(1 + \frac{1}{2}\pi_1 k_0)$ occurring in equation (5) calculated by me assuming the compression coefficient (k_0) of water at 0° to be 0.000050; and the fifth the percentage differences between the values in the two preceding columns.[2]

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[1] For data in regard to the volume change of other solutions see Arrhenius, Zeitschr. für physik. Chem., 10, 93.

[2] Owing to the error in sign previously referred to, the fourth column of the corresponding table published in my previous article (28, 223) contained the values of $V_0(1 - \frac{1}{2}\pi_1 k_0)$, and the percentage differences between those values and Dieterici's were much smaller than the correct ones which are given in this table.

Mols per Liter.	$\int_{p_1}^{p_0} vdp$	V_1	$V_0(1 + \frac{1}{2}\pi_1 k_0)$	**Percentage differences.**
0.607	23.66	0.999	1.000	0.1
1.040	47.32	0.997	1.001	0.4
1.903	97.07	0.990	1.002	1.2
2.681	164.6	0.989	1.004	1.5
3.792	297.8	0.979	1.007	2.8
4.908	456.8	0.970	1.011	4.1
5.598	575.8	0.967	1.014	4.7
8.164	1028.0	0.959	1.025	6.6
9.43	1301.0	0.958	1.032	7.4
11.69	1727.0	0.957	1.042	8.5
16.19	2693.0	0.947	1.064	11.7
22.18	4170.0	0.930	1.096	16.6

Since the values of the two volume-factors are essentially different from each other, it is evident that the osmotic pressures that would be obtained by dividing the integral by them would also differ, and that therefore one of the two methods of calculation must be inexact, or must refer to the osmotic pressure of the solution under a different condition. In view of the simplicity of the deductions given above, both by means of the cyclical process and the osmotic column, the question might well be considered decided in favor of the result thereby reached, at any rate until some real error is pointed out in my method of treatment. However, since Dieterici in his last article still maintains the correctness of the volume-factor representing the change of volume of the solution, it seems desirable to show by a consideration of a cyclical process involving that factor, the source of the error. A process of this kind has been employed for deriving the relation between osmotic and vapor pressures by previous authors, but they have intentionally left out of consideration the work done in compressing and dilating the solution and the variation of the osmotic pressure with the compression of the solution. This must not be done, however, if theoretically exact relations are to be derived.

7. DERIVATION OF THE RELATION BY MEANS OF A SECOND CYCLICAL PROCESS.

We will therefore consider the following completely reversible cyclical process, starting with one gram of solvent vapor of volume

v_1 and an indefinite large quantity of solution of volume $\omega - V_1$, these being in equilibrium with each other at the pressure p_1.

1. Condense the solvent vapor into the solution. Let its volume become thereby ω and its vapor pressure $p_1 + dp_1$. V_1 then represents the volume-factor above discussed, *i. e.*, the change in volume of the solution when one gram of solvent is added to an infinite quantity of it. The average pressure during these volume changes is $p_1 + \frac{1}{2}dp_1$.

2. Compress the solution until its pressure becomes such that it is in equilibrium with the pure solvent under its own vapor-pressure p_0, when placed in communication with it through a semipermeable wall. The external pressure must then become $p_0 + P_1' - dP_1'$, if $P_1' - dP_1'$ is the true osmotic pressure of the compressed solution. If the compression-coefficient of the solution is constant and equal to $k_1 + dk_1$, its volume after the compression is $\omega - \omega(k_1 + dk_1)(P_1' + p_0 - p_1 - dP_1' - dp_1)$. The average pressure under which this compression takes place is $\frac{1}{2}(P_1' + p_0 + p_1 - dP_1' + dp_1)$.

3. Force one gram of solvent out of the solution through the semipermeable wall. Let the volume of the pure solvent so obtained under the pressure p_0 be V_0. The external pressure on the solution becomes $p_0 + P_1'$ if the true osmotic pressure of the resulting solution is P_1'. If its compression-coefficient is constant and equal to k_1 its volume is $\omega - V_1 - (\omega - V_1)k_1(P_1' + p_0 - p_1)$. The average pressure under which the change of volume of the solution takes place is $P_1' + p_0 - \frac{1}{2}dP_1'$.

4. Expand the solution till its pressure becomes p_1. Its volume is then $\omega - V_1$; and it has returned to its initial condition. The average pressure under which this expansion takes place is $\frac{1}{2}(P_1' + p_0 + p_1)$.

5. Vaporize the one gram of solvent at the pressure p_0 (its volume then becoming v_0) and allow the vapor to expand till the pressure becomes p_1 and the volume v_1.

The cyclical process is now complete.

In order to calculate the work corresponding to the volume-changes of the solution in this process, the change of volume is to be multiplied by the average pressure under which it takes place, it being thereby assumed that the compression-coefficient is independent of the pressure. If the amounts of work done on the solution in the different parts of the process are thus calculated and added to the work done on the solvent, and their sum placed equal to zero, small quantities of the second order being neglected (noting however that those of the form $\omega d(-)$ are finite since ω is indefinitely large), the following equation is obtained:

$$\int_{p_1}^{p_0} v\,dp = (P_1' + p_0 - p_1)[V_1\{1 - \tfrac{1}{2}k_1(P_1' + p_0 - p_1)\} + \omega k_1 dp_1 - \tfrac{1}{2}\omega(P_1' + p_0 - p_1)dk_1].$$

In this equation the terms containing ω can be given a more readily intelligible form, if we designate the concentration of the solution of volume $\omega - V_1$ by c_1 and that of volume ω containing one gram more of solvent by $c_1 - dc_1$ and note that:

$$c_1 : c_1 - dc_1 = \omega : \omega - V_1$$

and therefore:

$$\omega = V_1 \frac{c_1}{dc_1}.$$

Substituting this value of ω, the last equation then becomes:

$$\int_{p_1}^{p_0} v\,dp = (P_1' + p_0 - p_1)V_1\left(1 - \tfrac{1}{2}k_1(P_1' + p_0 - p_1) + k_1 c_1 \frac{dp_1}{dc_1} - \tfrac{1}{2}c_1(P_1' + p_0 - p_1)\frac{dk_1}{dc_1}\right). \qquad (6)$$

In the special case where the vapor-pressure difference can be neglected in comparison with the osmotic pressure, this becomes:

$$\int_{p_1}^{p_0} v\,dp = P_1' V_1\left(1 - \tfrac{1}{2}k_1 P_1' - \tfrac{1}{2}c_1 \frac{dk_1}{dc_1} P_1'\right) \qquad (7)$$

8. COMPARISON OF THE RELATIONS DERIVED BY THE TWO CYCLICAL PROCESSES.

Equation (6) like equation (4) is rigidly exact, except in so far as error is introduced by the assumption that the compression-coefficient is independent of the pressure. The two equations are seen to differ with respect to all the quantities occurring in them except the vapor-pressures. Equation (6) is much more complex than equation (4), and has, moreover, one other characteristic which greatly diminishes its theoretical and practical value. Namely, it will be noted that it gives a relation between the osmotic pressure P_1' of a compressed solution when under the external pressure $(P_1' + p_0)$ and the vapor pressure of the same solution when under its own normal vapor pressure p_1 and that of the pure solvent also under its own normal vapor pressure p_0. In other words, it brings into relation the two kinds of properties measured under different external conditions of pressure. This fact alone is sufficient to make the result of little importance from a theoretical standpoint, and to show the unfitness of this ordinarily employed cyclical process as a means of deriving the exact value of the osmotic pressure P_1 at ordinary pressure, which is involved in almost all applications; such, for example, as the calculation of electromotive force. It is true, to be sure, that this osmotic pressure P_1' is the pressure that has been thus far experimentally determined by Pfeffer and others, no method having been yet found for producing the external negative pressure requisite in determining P_1 or for measuring directly the pressure on the semi-permeable wall itself.

It may be further pointed out that most of the other quantities occurring in equations (6) and (7) $\left(\text{namely } V_1, k_1, \text{and } \frac{dk_1}{dc_1}\right)$ vary with the concentration and nature of the solute, and must, therefore, be determined for each solution to which the formula is applied, while the corresponding quantities (V_0 and k_0) in equation (4) refer to the solvent, and hold true for any solution whatever in that solvent.

9. CONCLUSION.

It has been shown in this article by the consideration both of a new cyclical process and of the equilibrium-conditions of an osmotic column that the exact thermodynamic relation between the osmotic pressure (P_1) and vapor-pressure (p_1) of a solution is given by the equation:

$$\int_{p_1}^{p_0} v dp = (P_1 + p_0 - p_1) V_0 [1 + \tfrac{1}{2}(P_1 + p_0 - p_1) k_0]$$

in which p_0, V_0, and k_0 are the vapor-pressure, specific volume, and compression-coefficient respectively of the liquid solvent. The only simplifying assumption made in the derivation of this equation was that k_0 could be regarded as constant between the pressures p_0 and $p_1 - P_1$, the latter pressure being in general negative. Since the value of the term containing the compression-coefficient (k_0) is very small, even for fairly high concentrations, the approximate osmotic pressure of a solution is correctly calculated by dividing the vapor-pressure integral by the ordinary specific volume of the solvent, and not, as has been generally done heretofore, by dividing it by the volume-change of the solution. It has also been shown that the derivation by the cyclical process heretofore employed, when rigidly carried out, is far less simple in character, and gives as a result a more complex relation, which involves, moreover, the osmotic pressure of the compressed solution, not that of the solution under its own pressure, and a number of other quantities which have to be determined specifically for each solution to which the equation is applied, instead of determining them for the solvent, once for all.

POSTSCRIPT.

The beautiful investigation of Worthington on "The Mechanical Stretching of Liquids: an Experimental Determination of the Volume-Extensibility of Ethyl Alcohol" (Philos. Trans. of the Royal Society, 183, pp. 355–370. 1892) first came to my attention while reading the proof of the foregoing article. This investigation has demonstrated the possibility not only of realizing high negative pressures (up to 17 atmospheres), but also even of measuring the dilatation-coefficient with a fair degree of accuracy. It has also proved, in the words of the author, that "in the neighborhood of zero pressure the absolute coefficient of volume elasticity of alcohol is the same for extension as for compression, and, so far as the observations show, is constant between a pressure of + 12 and − 17 atmospheres." Any hypothetical element which may have been thought to be involved in the deduction given in the preceding article by reason of the employment of negative pressures is, therefore, to a great extent, removed; and in applications of the derived equation the value of the compression-coefficient measured for small positive pressures can be generally employed with a much greater degree of confidence, in view of the demonstrated constancy of the coefficient for positive and negative pressures in the case of one liquid.

Massachusetts Institute of Technology,
Boston, Mass., November, 1900.

DEPENDENCE OF THE MODULUS OF TORSION ON TENSION.

By J. R. Benton.

It is to be expected from the theory of elasticity that the coefficients of elasticity of a body should vary as it is deformed. If X_x, Y_y, Z_z, denote the normal components of stress on planes perpendicular respectively to the X, Y and Z axes of coördinates; Y_z, Z_x, X_y, the tangential components on the same planes; and x_x, y_y, z_z, y_z, z_x, x_y, the corresponding components of strain; then the relation between stress and strain can be written in the general form

$$\begin{aligned} X_x &= f_1(x_x, y_y, z_z, y_z, z_x, x_y) \\ Y_y &= f_2(x_x, y_y, z_z, y_z, z_x, x_y) \end{aligned} \tag{1}$$

with similar formulas for the other components of stress. f_1, f_2 denote unknown functions. If these functions are developed according to Maclaurin's formula, we have

$$\begin{aligned} X_x = c_{11}x_x + c_{12}y_y + c_{13}z_z + c_{14}y_z + c_{15}z_x + c_{16}x_y + d_{11}x_x^2 + d_{12}y_y^2 \\ + \cdots + d_{17}\cdot 2x_xy_y + \cdots + e_{11}x_x^3 + \cdots \\ Y_y = c_{21}x_x + c_{22}y_y + \cdots + d_{21}x_x^2 + \cdots \end{aligned} \tag{2}$$

with similar equations for Z_z, Y_z, Z_x, and X_y; the c's, d's, e's, etc., denote constants. The constant term $f(0)$, which is usually placed at the beginning of Maclaurin's series, is omitted, because it is assumed that the stress disappears when all the strains disappear. The strains are exceedingly small quantities in comparison with the stresses; it is therefore customary to neglect their squares and products, and to break off the series (2) after the sixth term. The resulting equations form the basis of the ordinary theory of elasticity; they make the strains proportional to the stresses, the coefficients remaining unchanged as the strains increase indefinitely.

If, however, the strains are so large or so accurately known that their squares cannot be neglected, then the series (2) must include the terms of the second degree. This gives

$$\begin{aligned} X_x = (c_{11} + d_{11}x_x + d_{17}y_y + d_{18}z_z + d_{19}y_z + d_{110}z_x + d_{111}x_y)x_x \\ + (c_{12} + d_{12}y_y + d_{17}x_x + d_{112}z_z + d_{113}y_z + d_{114}z_x + d_{115}x_y)y_y \qquad (3) \\ + (c_{13} + \cdots)z_z + (\cdots)y_z + (\cdots)z_x + (\cdots)x_y \end{aligned}$$

and similar expressions for Y_y, Z_z, Y_z, Z_x, X_y. It is evident that the proportionality between stress and strain no longer subsists. In place of the ordinary coefficients of elasticity the *c*'s of our formulas, we have the expressions in ( ) in (3); the latter fill exactly the place of the *c*'s in the ordinary theory of elasticity, and can therefore be regarded as new coefficients of elasticity which, however, depend on the strain and therefore vary as the body is deformed.

The theory of the dependence of the coefficients of elasticity on the deformation in the case of a homogeneous, isotropic body, has been worked out in two forms. Voigt,[1] assuming that the strains can be neglected in comparison to the size of the body, deduced formulas which represent the behavior of a homogeneous, isotropic body by means of three new constants of elasticity in addition to the two of the usual theory. Jos. Finger,[2] independently of Voigt, investigated the same problem, but did not neglect the strain in comparison to the size of the body. He arrived at formulas which contain four new constants, besides the two of the old theory of elasticity.

Experiments have verified the theory, and shown that the coefficients of elasticity depend in a slight degree on the deformation, even far within the elastic limit, and that, therefore, the strain is not exactly proportional to the stress. This seems to have been known as early as 1705, when James Bernouilli[3] wrote: "Des fibres homogènes de même longueur et largeur, mais chargées de differents poids, ne s'étendent ni se compriment pas proportionellement à ces poids;

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[1] W. Voigt, Wiedemann's Annalen, 52, p. 536, 1894.

[2] Jos. Finger, Wiener Berichte, Band 103, Abth. IIa, 163, 1894.

[3] J. Bernouilli, Gesammelte Werke, Band II., 976–989. Geneva, 1744. Quoted in Todhunter and Pearson, History of the Theory of Elasticity and of the Strength of Materials. Cambridge, 1886.

mais l'extension ou la compression causée par le plus grand poids, est à l'extension ou la compression causée par le plus petit, en moindre raison que ce poids-là n'est à celui-ci." During the present century numerous experiments on the elasticity of extension, especially those of Eaton Hodgkinson[1] on structural iron and steel, and those of J. O. Thomson[2] on wires of various metals, have shown that for most substances the increase of length is not exactly proportional to the stretching force.

On the other hand, Voigt's careful experiments on the torsion and flexure of crystals failed to show any deviation from proportionality, although he carried the deformations almost to the breaking point. This result, however, follows from Voigt's development of the theory of the dependence of elastic constants on deformation; according to which the deviation from proportionality appears in a term of the first order in the case of extension, but in a term of the second order in the cases of torsion or flexure.

The modulus of torsion, then, according to theory, does not vary appreciably with the torsion; it does vary appreciably, however, with the extension in the direction of the axis of torsion. The theory enables us to express the modulus of torsion in terms of the tension in the direction of the axis. If m denote the modulus, P the tension, and α, β, γ be constants, then

$$m = \alpha + \beta P + \gamma P^2. \tag{4}$$

This formula follows from the theory, both under Voigt's assumption that the strains can be neglected with respect to the dimensions of the body, and under Finger's assumption that they cannot; only the constants have a somewhat different meaning in the two cases. In both cases α is the ordinary modulus of torsion, when no tension is present; β and γ are rather complicated functions of the five (according to Voigt) or six (according to Finger) elastic constants of the substance in question. The mathematical details of the deduction of the above formula may be left out here.[3]

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[1] E. Hodgkinson, Report of the Commission appointed to enquire into the Application of Iron to Railway Structures. London, 1849, pp. 47–67.

[2] J. O. Thomson, Wiedemann's Annalen, 44, p. 555, 1891.

[3] The mathematical deduction will be found in the Göttingen Dissertation—"Abhängigkeit der specifischen Torsionswiderstandes einiger Metalldrähte von der Spannung." J. R. Benton, 1900.

The results of the experiments described below were found to agree well with this formula.

The experimental investigation of the changes of the modulus of torsion with the tension was suggested by Lord Kelvin[1] in 1878, but no experiments were made until those of Cantone and Michelucci[2] in 1897. They used wires of iron, copper, brass, nickel, and silver, which hung vertically, and were twisted by means of horizontal pulleys at the bottom of the wires. The wires were repeatedly loaded and unloaded, and the change of the angle of torsion at each change of load observed. Experiments were made with different values for the original angle of torsion. It was found that an increase of tension was accompanied by an increase of the angle of torsion, therefore by a decrease of the modulus of torsion. Nickel, however, behaved exactly oppositely to the other wires. Cantone and Michelucci did not attempt to formulate a law for the variation of the modulus of torsion; and they seem to have left out of account the influence of the change of shape of the wire when loaded; the fact of its becoming longer and thinner would change its amount of torsion, even if the modulus remained the same.

It was suggested to me by Professor Voigt to investigate the subject more exhaustively, using more exact methods. The experiments described here were made in his laboratory in the University of Göttingen.

The method used to determine the modulus of torsion under the various tensions consisted in comparing, by means of the method of coincidences, the period of torsional vibration of a disk fastened to the wire, with the period of a pendulum swinging in front of the disk.

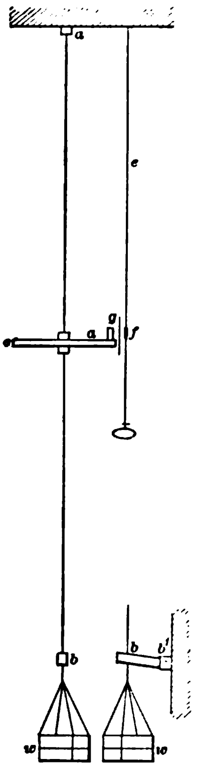

Fig. 1.

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[1] Lord Kelvin, Article "Elasticity" in the Encyclopedia Britannica.

[2] M. Cantone and E. Michelucci, Rendiconti della reale Accademia dei Lincei (5), 6, pp. 191–198, 1897.

A wire about three meters long was fastened firmly to the ceiling of the room by means of the clamp *a* (Fig. 1). The lower end of the wire was clamped in the end of the arm *b*, about 8 cm. long, which was free to turn about a horizontal axis *b*′. In this way the extension of the wire was not interfered with, while sidewise motion of the lower end was prevented, and the torsion was limited to the the space between *a* and *b*. Exactly in the middle of this space a brass disk *c*, 18 cm. in diameter, was fastened. For wires of different thicknesses I used disks of different weights, ranging from 0.7 kg. to 2.2 kg.

The disk made torsional vibrations. The tension of the wire was produced by means of weights hung on below the arm *b*. I took special pains to see that the points at which the wire was clamped in *a* and *b* did not change when the wire contracted as a result of the tension.

On the edge of the disk *c* a little piece of sheet iron *d*, about 1 cm. high, and bent to a right angle, was set up vertically. The two sides of the angle made equal angles with the radius of the disk, so that the resistance of the air was the same when the disk swung in one direction as when it swung in the other; one side was painted white so as to be distinctly visible, the other side was blackened. The white side was strongly illuminated (when the disk was in its position of rest) by the light of a gas burner concentrated by means of a lens. The whole angle *d* was movable along the edge of the disk, and could be set where it was wanted.

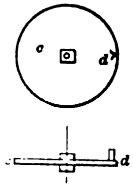

Fig. 2.

In front of the disk hung a pendulum, consisting of a lens-shaped piece of lead hung on a fine steel wire. At the same height as the angle *d*, this fine wire carried a little black cylinder *f*, of such a diameter that it just covered the white side of the angle *d*, when looked at in the horizontal line passing through the pendulum wire and the wire to be investigated. Between the disk and the pendulum wire was a black screen *g*, with a rectangular hole in it of just the same breadth as the diameter of the cylinder. When the pendulum and disk were at rest, the centers of the wire, the white half of the angle *d*, the hole in the screen, and the black cylinder were all in the same straight line. A telescope was set up in that line at a distance of about three meters from the wire, so that the vibrations of the pendulum and disk could be observed from a distance.

The length of the pendulum was so adjusted that its period T was nearly equal to that of the torsional vibrations of the disk (or else $2T$ or $3T$ were made nearly equal to the period of the disk, in cases where it swung more slowly). The coincidences were observed through the telescope; a coincidence taking place when the black cylinder f passed the hole in the screen g at the same time (and in the same direction) as the illuminated side of the angle d, and hid the latter from view. A perfect coincidence rarely took place; the cylinder f usually left part of the bright angle uncovered; at one swing the bright part appeared on one side, at the next on the other side of the cylinder. It was possible, however, by watching a few swings before and after the coincidence, to estimate in tenths of a pendulum swing, the true time of the coincidence.

If θ is the interval between two successive coincidences, the period S of the disk is given by

$$S = \frac{\frac{\theta}{T}}{\frac{\theta}{T} \pm 1} \cdot T = \frac{\theta}{\theta \pm T} \cdot T \tag{5}$$

It will be seen that an error of the first order in T appears only in the second order in $\frac{\theta}{\theta \pm T}$, so that the period of the disk *in terms of* T can be determined very accurately when T is known only approximately. T was determined by measuring three times with a stop-watch (reading to 0.2 second) the time of 100 swings of the pendulum. The error of T may be taken as $\pm$ 0.002 second; that of $\frac{\theta}{\theta \pm T}$ is then $\frac{\mp 0.002\theta}{(\theta \pm T)^2}$. If T remains the same for the different determinations of S under different tensions of the same wire, the values of S can be compared very accurately without the necessity of a very accurate determination of T.

The length of the pendulum was so adjusted that a coincidence occurred about every two and one-half minutes.

The pendulum lost its motion very slowly, and an amplitude of more than one and one-half degrees was never given to it, so that its period could be regarded as absolutely constant. The variations of its period during a series of observations must have amounted to less than a thousandth of one per cent. The period of the disk, on the contrary, varied considerably with the amplitude for most wires. The causes of this variation—resistance of the air, internal friction of the wire, adiabatic temperature changes due to the deformation, and a possible variation of the elasticity with the angle of torsion—were so complicated that it did not seem practicable to investigate them separately; the dependance of the period on the amplitude was therefore determined empirically. This was done by making a long series of observations as the amplitude died away. It was found that the time θ between two coincidences could be represented with very close approximation as a linear function of the amplitude A.

$$\theta = \theta_0 + bA. \tag{6}$$

This empirical result holds true up to about 50°, but the amplitudes in my experiments never exceeded 35°, and usually lay between 10° and 20°.

Thermometers were placed at the top, the middle, and the bottom of the wire, and the temperature was measured by them, and kept constant within about 2° by opening or closing a door which led to a cooler room. Sudden currents of air were avoided.

Each wire, soon after it was hung from the ceiling, was heated twice to dull redness by means of a Bunsen burner, under the greatest safe load, in order to make it hang straight. After it had cooled, it was loaded to somewhat more than the greatest load to be used in the experiments, and left hanging free for one to two days. Then it was clamped at the bottom, and the observations were begun.

In order to determine the period of the disk when the wire was under any given tension, a series of ten coincidences was observed. For some wires, however, the vibration died down so rapidly that I had to be satisfied with seven coincidences; while for some others the amplitude remained so nearly constant that the observations had to be continued for 15 or 20 coincidences, in order to determine the effect of the amplitude on the period. At each coincidence the time was determined by means of a stop-watch (the difference of the observed, approximate coincidence from the true coincidence being estimated), and the amplitude of the disk was observed by means of a scale of angles marked on its edge. To determine the period at the amplitude zero, equations of the form (6) were set up, and the constants θ_0 and b determined from them by the method of least squares. θ_0 is the time between two coincidences at the amplitude zero; from it the period S of the disk was calculated, in terms of the period T of the pendulum.

The modulus of torsion m is given by the equation

$$m = \frac{2\pi K}{S^2} \cdot \frac{l}{r^4} \tag{7}$$

where K is the moment of inertia of the disk and wire, l is the length, and r the radius of the wire. To use this formula an accurate knowledge of T and K is necessary. But inasmuch as I was investigating only the *changes* of the modulus of torsion, and not its absolute value, I simply compared m with m_s, the modulus of torsion under a standard load; T and K, of course, remained the same. This gives

$$\frac{m}{m_s} = \frac{S_s^2 l r_s^4}{S^2 l_s r^4}, \quad \text{or} \quad m = \left(\frac{S_s}{S}\right)^2 \cdot \left(\frac{l}{l_s}\right) \cdot \left(\frac{r_s}{r}\right)^4 \cdot m_s. \tag{8}$$

The changes of l and r are those due to the linear extension and the lateral contraction of the wire when loaded. $\frac{l}{l_s}$ was determined by direct observation. A needle was fastened to the lower end of the wire and the distance through which it moved as the wire was loaded was read by means of a microscope with micrometer screw-head. The quantity $\frac{r_s}{r}$ was also determined directly, the contraction of the wire being measured by means of an interference apparatus. For a detailed account of the method used, see Article: "Determination of Poisson's Ratio by Means of an Interference Apparatus," Phys. Rev. $\frac{l}{l_s}$ and $\frac{r_s}{r}$ were very slightly different from unity, so that it was possible to assume Hooke's law, and regard the deformation as proportional to the tension.

Each wire was observed under five different tensions; three series of observations were made; first one beginning with the smallest tension, and increasing the tension continuously to the greatest; then one beginning with the greatest and decreasing continuously to the smallest; finally one beginning with the smallest again. Thus fifteen determinations were made with each wire, each determination consisting in the observation of a series of coincidences.

The results obtained are given in the tables below. The first column gives the substance of the wire, the second column its diameter in millimeters, the third the loads in kilograms, the fourth the tensions produced by them in kilograms per square millimeter; the fifth and sixth columns give the modulus of torsion in terms of the modulus of torsion under (an assumed) standard tension, the fifth as observed and the sixth as calculated from the formula (4). The seventh column gives the approximate absolute value of the modulus of torsion.

Substance.	Diameter.	Load.	Tension.	Modulus of Torsion.		
				Observed.	Calculat'd.	Absolute value.
Steel	0.685	2	5.43	1.00364	1.00362	7.523×10^{11}
		5	13.57	1.00219	1.00243	
		10	27.14	1.00000	0.99979	
		15	40.71	0.99608	0.99633	
		18	48.85	0.99386	0.99386	
Steel..........................	1.000	10	12.73	1.00242	1.00247	8.077×10^{11}
		15	19.10	1.00120	1.00119	
		20	25.46	1.00000	0.99997	
		24.7	31.45	0.99897	0.99886	
		29.4	37.43	0.99772	0.99780	
Steel..........................	1.405	10	6.45	1.00134	1.00142	8.030×10^{11}
		15	9.68	1.00059	1.00059	
		20	12.91	1.00000	0.99993	
		24.7	15.95	0.99949	0.99940	
		29.4	18.98	0.99894	0.99902	
Iron	0.883	3	4.89	1.00173	1.00213	5.671×10^{11}
		6	9.84	1.00185	1.00131	
		9	14.68	1.00000	0.99983	
		12	19.57	0.99771	0.99820	
		15	24.47	0.99600	0.99589	

Substance.	Diameter.	Load.	Tension.	Modulus of Torsion.		
				Observed.	Calculat'd.	Absolute value.
Iron	1.190	5	4.50	1.00126	1.00126	6.372×10^{11}
		10	9.00	1.00058	1.00065	
		15	13.49	1.00000	0.99998	
		20	17.99	0.99932	0.99928	
		25	22.49	0.99859	0.99856	
Iron	1.578	10	5.00	1.00088	1.00090	6.732×10^{11}
		15	7.51	1.00063	1.00057	
		20	10.01	1.00000	1.00026	
		25	12.51	1.00042	0.99996	
		30	15.02	0.99963	0.99971	
Copper	0.947	2	2.84	1.00490	1.00501	7.057×10^{11}
		4	5.68	1.00400	1.00340	
		6	8.51	1.00000	1.00060	
		8	11.35	0.99659	0.99651	
		10	14.19	0.99058	0.99072	
Copper	1.390	2	1.32	0.99997	1.00000	6.139×10^{11}
		5	3.30	1.00027	1.00030	
		10	66.59	1.00000	0.99986	
		15	9.89	0.99803	0.99824	
		18	11.86	0.99680	0.99669	
Copper	1.728	10	4.24	1.00252	1.00122	5.342×10^{11}
		15	6.37	1.00077	1.00120	
		20	8.49	1.00000	1.00050	
		25	10.61	0.99753	0.99891	
		30	12.73	0.99760	0.99651	
Nickel	0.818	2	3.72	0.99581	0.99504	8.952×10^{11}
		5	9.29	0.99585	0.99610	
		10	18.58	1.00000	1.00000	
		15	27.87	1.00735	1.00644	
		18	33.44	1.01054	1.01130	
Nickel	0.963	2	2.74	0.99513	0.99489	9.026×10^{11}
		5	6.86	0.99649	0.99685	
		10	13.73	1.00000	1.00004	
		15	20.59	1.00352	1.00309	
		18	24.71	1.00463	1.00487	
Nickel	1.490	10	5.73	0.99734	0.99688	5.518×10^{11}
		15	8.60	0.99822	0.99862	
		20	11.47	1.00000	1.00014	
		25	14.34	1.00134	1.00147	
		30	17.20	1.00278	1.00258	
Brass	0.787	2	4.11	1.00384	1.00417	3.688×10^{11}
		5	10.28	1.00169	1.00173	
		8	16.44	1.00000	0.99917	
		11	22.61	0.99573	0.99641	
		14	28.77	0.99353	0.99343	

Substance.	Diameter.	Load.	Tension.	Modulus of Torsion.		
				Observed.	Calculat'd.	Absolute value.
Brass	0.943	2	2.87	1.00110	1.00111	3.855 × 10^{11}
		4	5.74	0.99980	1.00050	
		6	8.60	1.00000	0.99993	
		8	11.47	0.99948	0.99933	
		10	14.34	0.99852	0.99870	
Brass	1.498	7	3.97	1.00057	1.00058	3.804 × 10^{11}
		10	5.67	1.00037	1.00038	
		15	8.51	1.00000	0.99999	
		20	11.35	0.99951	0.99953	
		22.8	12.94	0.99926	0.99925	
Nickelin	0.795	2	4.03	1.00946	1.00943	5.921 × 10^{11}
		5	10.07	1.00559	1.00571	
		10	20.14	1.00000	0.99987	
		15	30.21	0.99444	0.99449	
		18	36.24	0.99146	0.99147	
Nickelin	0.978	2	2.66	1.00410	1.00426	6.166 × 10^{11}
		5	6.65	1.00300	1.00270	
		10	13.31	1.00000	0.99998	
		15	19.96	0.99677	0.99711	
		18	23.96	0.99554	0.99531	
Nickelin	1.397	10	6.52	1.00144	1.00140	6.573 × 10^{11}
		15	9.78	1.00063	1.00071	
		20	13.05	1.00000	1.00011	
		25	16.31	0.99989	0.99961	
		30	19.57	0.99908	0.99921	
German silver	1.005	2	2.53	1.00417	1.00417	7.451 × 10^{11}
		5	6.33	1.00271	1.00270	
		10	12.67	1.00000	0.99999	
		15	19.00	0.99690	0.99694	
		18	22.81	0.99500	0.99496	
German silver	1.592	10	5.02	1.000526	1.000522	6.584 × 10^{11}
		15	7.53	1.000232	1.000245	
		20	10.05	1.000000	0.999986	
		25	12.56	0.999736	0.999742	
		30	15.07	0.999516	0.999515	
Brass with large percentage of copper.	0.996	2	2.57	1.00318	1.00320	3.804 × 10^{11}
		5	6.42	1.00280	1.00310	
		10	12.84	1.00000	0.99943	
		15	19.26	0.99126	0.99140	
		18	23.11	0.98445	0.98460	
Bronze	0.902	2	2.82	1.00451	1.00437	9.077 × 10^{11}
		4	5.65	1.00158	1.00196	
		6	8.47	1.00000	0.99972	
		8	11.30	0.99762	0.99762	
		10	14.12	0.99565	0.99570	

From the above observations the following values of β and γ in the formula $m = \alpha + \beta P + \gamma P^2$ result. 1 kg. per square mm. is taken as the unit of tension.

Substance.	Diameter of Wire.	Modulus of Torsion.	
		Observed.	Calculated.
Steel	0.685	−0.000104	−0.00000222
	1.000	−0.000218	+0.00000061
	1.405	−0.000367	+0.00000698
Iron	0.883	+0.000011	−0.0000105
	1.190	−0.000127	−0.0000007
	1.595	−0.000149	+0.0000013
Copper.	0.947	+0.000168	−0.0000843
	1.390	+0.000406	−0.0000545
	1.792	+0.001042	−0.0000895
Nickel	0.818	+0.000022	+0.0000135
	0.963	+0.000493	−0.0000013
	1.490	+0.000788	−0.0000126
Brass	0.787	−0.000339	−0.00000275
	0.943	−0.000360	−0.00000099
	1.498	−0.000082	−0.00000039
Nickelin	0.795	−0.000639	+0.00000220
	0.978	−0.000371	−0.00000175
	1.397	−0.000285	+0.00000449
German silver	1.005	−0.000305	−0.00000407
	1.592	−0.000126	+0.00000131
Brass with large percentage of copper.	0.996	+0.000439	−0.0000524
Bronze.	0.902	−0.001961	+0.0000397

These results differ for wires of different thickness of the same material. This must be due to the inhomogeneity of the surface, which would have a greater effect on thin wires than on thick ones. It is well known that working the surface of metals has a marked effect on their elasticity. The drawing of a wire must affect its surface; besides which the surface absorbs gases and vapors, and it is the seat of chemical action, the products of which it is not easy to entirely remove. The wires of different sizes give quite different values for the modulus of torsion, so that it is not surprising that the values of β and γ also vary.

The values found then, cannot be taken as universal constants for the substance in question, but must be regarded simply as constants which give the behavior of particular wires. As the thickness of the wires is increased, β and γ approach values which must be the universal ones for the substance in question. So that by a consideration of the change of β and γ with increasing diameter of the wire, it is possible to obtain a certain amount of knowledge about them. They may be either positive or negative; β probably never exceeds 0.001 m_t and is generally much less, γ is less than 0.00005 m_t. The algebraic sign of β and γ for the different substances is as follows:

Steel.	$\beta-$	$\gamma+$
Iron.	$-$	$+$
Copper.	$+$	$-$
Nickel.	$+$	$-$
Brass.	?	?
Nickelin.	$-$	$+$
German silver.	$-$	$+$

It is not possible to investigate the dependence of the modulus of torsion on tension outside of rather narrow limits. The tension can not exceed the limit of elasticity on the one hand; on the other hand it is not practicable to carry on the investigation with negative tensions, as this would necessitate the use of short thick bars, where a uniform distribution of the stress over the end surface is almost unattainable. Between the tension zero and the elastic limit, the present investigation shows that the law

$$m = a + \beta P + \gamma P^2$$

holds true within the limits of error of the experiments, and that the different substances used behave in the following way: Both steel and iron have negative β and positive γ, which, however, is so small that β alone determines their behavior. Their modulus of torsion decreases therefore, as the tension increases. Copper, and brass with a large percentage of copper, have positive β and negative γ; the latter is large enough to determine their behavior for moderate tensions. The modulus of torsion first increases a little, then decreases quickly. The modulus of torsion reaches a maximum when the tension is about 6 kg. per mm^2. Nickel has positive β and very small negative γ. Its modulus of torsion increases as the tension increases, as Cantone and Michelucci[1] also found. Nickel is the only one of the substances I investigated, which has this property up to the limit of elasticity. For brass both β and γ are very nearly zero, so that the modulus of torsion varies only slightly with the tension. Nickelin has negative β and very small positive γ; its modulus of torsion decreases with increasing tension. For German silver β is negative, γ positive and small; its modulus of torsion also decreases with the tension. For bronze I have not enough observations to draw conclusions about the universal constants.

To sum up the results of this investigation we may say:

1. That a dependence of torsional elasticity on tension, which is to be expected from the theory, actually occurs.

2. That this dependence can be expressed, within the limits of error of the observations, by the law $m = a + \beta P + \gamma P^2$, where m is the modulus of torsion, P the tension, and a, β, γ are constants.

3. That on account of the inhomogeneity of the surface of the wires, no conclusion about the constants for the substance in question can be drawn from observations on a single wire; but the values of β and γ obtained from such observations represent merely the behavior of the individual wire.

4. That in spite of this, observations of a series of wires of the same substance and different diameters make it possible to draw conclusions about the universal constants for the substance. It is found accordingly that the modulus of torsion of steel, iron, brass (when it does not contain too much copper), nickelin and German silver decreases with increasing tension; that that of copper, and brass containing much copper, at first increases and then decreases; that that of nickel increases continuously. This holds between the tension zero and the limit of elasticity.

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[1] Rendiconti della reale Accademia dei Lincei (6), pp. 191–198, 1897.

A DETERMINATION OF THE VISCOSITY OF WATER.

By E. R. Drew.

THE apparatus used in this investigation is an attempt to realize as nearly as possible the ideal condition from which is obtained the conception of coefficient of viscosity, namely, that of a liquid contained between two parallel planes of infinite extent, one of which is moving in a direction parallel to the other, with constant velocity. It consists essentially of two vertical coaxial cylinders, the outer capable of rotating at any desired speed, while the inner, which is closed at the ends, is suspended by means of a torsion wire between agate bearings in the axis. The liquid used is contained in the space between the two cylinders.

The idea of coaxial cylinders was used for the same purpose by Professor Perry ("Liquid Friction," Phil. Mag., 35–441, 1893), who has given the complete mathematical theory, provided the effect due to the lower end of the suspended cylinder may be neglected or allowed for. The apparatus here used was constructed by Mr. E. L. Johonnott, under the direction of Professor Michelson; and as they were at the time unacquainted with the work of Perry, the idea was carried out in a quite different manner. Mr. Johonnott had completed the apparatus, and obtained some preliminary observations, when his attention was called to other lines of work, and the continuation of the investigation was intrusted to the writer by Professor Michelson.

The main object in view was to obtain a result which could be compared with those which have been obtained by the very different method, due to Poiseuille, of flow through capillary tubes.

Fig. 1 is a section through the axis of the instrument. The inner cylinder, *A*, is held in position by two agate bearings *b*, *b*, by means of which it can be centered with considerable accuracy. The torsion wire is attached to the cylinder by means of the rigid brass frame *F*, which passes around the heavy cross-bar carrying the upper bearing. When in use, the bearings and suspending wire are so adjusted as to give an amount of side play barely perceptible to the touch, in each bearing. The effects of friction in the bearings are then inappreciable. Deflections are read with telescope and scale, the latter in the form of an arc of a circle about the suspending wire as center.

The inner cylinder was accurately turned; but as the inner surface of the outer cylinder could not readily be turned, with the facilities at hand, selected pieces of brass tubing which were very nearly cylindrical were used, and an attempt made to experimentally determine the error introduced. The outer cylinder is surrounded by a water-jacket, not shown in the figure, which allows the temperature of the liquid used to be readily determined, and aids in keeping it steady.

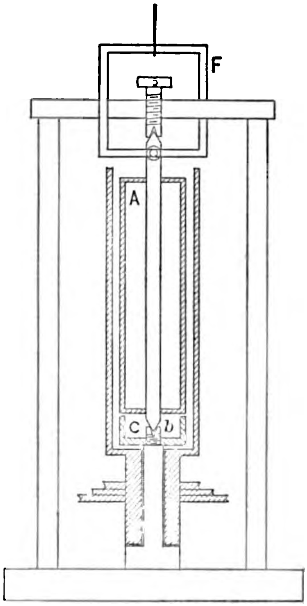

Fig. 1.

An ingenious and simple chronograph attachment, also not shown, was devised by Mr. Johonnott, to record the number of turns per second made by the outer cylinder during the time of an observation. Power was at first obtained from an engine in the mechanician's shop, but the speed was not sufficiently steady, and a 1-h.-p. electric motor was substituted, which, with a heavy balance-wheel on the countershaft, gave good satisfaction.

C is a brass cup screwed on the central shaft, with its upper edge almost in contact with the lower end of the suspended cylinder. It was found in practice that the water which filled the space between the cylinders seldom entered the cup. It was expected that this device would eliminate the effect, previously referred to, due to the lower end of the cylinder. When the cylinder had attained its equilibrium position, due to a steady rotation of the outer cylinder, the cup would form practically a continuation of the cylinder, of considerable length as compared with the thickness of the layer of liquid. Then the effect at a point near the lower end of the cylinder should be nearly or quite the same as at a point on an infinitely long cylinder, and Perry's analysis would apply directly.

A large number of observations showed that the deflection did not increase exactly with the speed, as it should, but somewhat faster. An example will show the magnitude of the effect. The speed is given under n, number of turns per second, and D is the deflection in cm. on the scale.

n	D	D/n
3.63	1.39	.383
5.20	2.01	.387
8.42	3.36	.399
10.61	4.37	.412
13.55	5.72	.422

To see whether this was in any way due to the free surface of the liquid, which was always set just at the upper edge of the suspended cylinder, a cup similar to C was suspended from the cross-bar, to form a continuation of the cylinder, and the free surface of the water raised some distance. The results then obtained showed no appreciable improvement. Subsequent experiments conducted along various lines seemed to indicate that the trouble was at the lower end of the cylinder, but no decisive result could be reached.

A little consideration showed that in order to apply the simple theory, as is done in Perry's discussion, the essential condition which must be fulfilled is that, when steady motion has been attained, all the points in the liquid which have a common speed must lie in a surface which, within the region considered, is everywhere equidistant from the bounding surfaces. Thus the surface of mean speed, in the case of a liquid contained between two planes, is a plane half way between them. In the present case, it is evident that the surface of mean speed will enter the angle P, Fig. 2, at an inclination of about 45° to the vertical, as shown by the dotted line, and will probably be displaced from its proper position for some distance above the lower end of the inner cylinder. If this displacement varies with the speed, the results obtained are accounted for.

The difficulty was overcome by means of the arrangement shown in Fig. 3. The two rings, shown in section at r and s, are attached, one to the outer cylinder, the other to the cup. The slant face of *s* is then fixed, while that of *r* moves with the outer cylinder, so that the vertical line midway between them represents the surface of mean speed. This is not exactly true, since different portions of the slant face of *r* move with different speeds; but with the dimensions used, the error from this cause is small. With this arrangement the results at different speeds show no consistent difference.

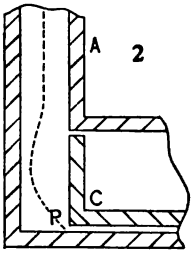

Fig. 2.

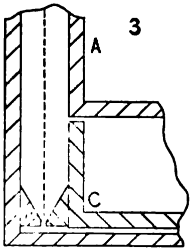

Fig. 3.

The torsion constant of the suspending wire, defined as the force in dynes which must be applied at the surface of the cylinder, in a direction perpendicular to the axis, to produce a deflection of 1 cm. as read on the scale, was determined in two ways. The first method was that of the torsion pendulum, which took the form of a horizontal brass bar attached at its center to the lower end of the frame *F*. Near its ends, and equidistant from the center, two equal brass cylinders, with their axes vertical, were attached in such a way that they could be easily removed and replaced in the same position.

Following are the data for this determination:

Period of vibration, cylinders in position.	4.131 sec.
" " " " removed.	2.811 "
Moment of inertia of cylinders in position.	13780 gram-cm^2.
Radius of suspended cylinder *A*.	2.300 cm.
Scale distance.	76.52 cm.
Torsion constant, as previously defined.	161.3 dynes.

The plan of the second method is shown in Fig. 4; *acd* is a very fine silk fiber, one end of which is wound around the upper end of the suspended cylinder, the outer cylinder and the bearings having been removed. The other end is wound around a pin at *a*, and a small mass *m* is hung from *c* by a similar fiber. A third fiber is hung from *a* to serve as a plumb-line. The pin at *a* is attached to an arm pivoted near *c*, so that different inclinations of *ac* may be used. The portion *cd* of the fiber is brought to the horizontal each time by winding on the pin at *a*. The distances *ab* and *bc* are readon millimeter scales, and the horizontal force calculated. This force pulled the suspending wire out of the vertical, and slightly increased the scale-distance, from 76.52 cm. to 76.70 cm. in the extreme case, and this was allowed for in calculating results.

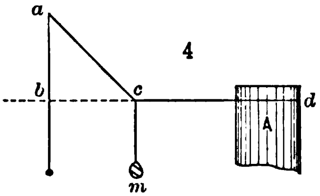

Fig. 4.

Torsion constant, mean of ten determinations, 161.4 dynes.

Greatest difference between two determinations, 0.6 dyne.

Two outer cylinders, of different diameters, were used. As they were not truly cylindrical, 16 equally-spaced diameters were measured at each end.

Dimensions of cylinders.	Outer Cylinder No. 1.	Outer Cylinder No. 2.	Inner Cylinder.
Mean radius, R_1.	2.538 cm.	2.851 cm.	R_2, 2.300 cm.
Greatest difference between two radii.	0.0023 cm.	0.015 cm.	
Length, L.			25.30 cm.

The final determinations were made at temperatures which seldom differed by more than 0°.2 from 20°, and the results were reduced to 20° by the formula computed by Helmholtz from Poiseuille's observations.[1]

$$\mu = \frac{0.0178}{1 + .0337t + .0022t^2}.$$

Observations were made at speeds of about 4, 6 and 8 turns per second. The result computed from each observation is the ratio D/n, the deflection which would be produced at a speed of one turn per second. These results are here summarized:

Outer Cylinder, No. 1.

Mean of 33 observations.	$D/n = 1.615$
Greatest difference.	0.012
Average deviation from mean.	0.0031

Outer Cylinder, No. 2.

Mean of 26 observations.	$D/n = 0.821$
Greatest difference.	0.009
Average deviation from mean.	0.0018
Scale distance.	76.18 cm.
Torsion constant of wire reduced to this distance.	160.6 dynes.

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[1] See O. E. Meyer, Wied. Ann., 1877, p. 391.

The formula reached by Perry is

$$M = 4\pi\mu\omega R_1^2 R_2^2 / (R_1^2 - R_2^2)$$

where ω is the angular velocity of the outer cylinder, and M is the moment per unit length of the suspended cylinder, exerted upon its surface by a liquid for which μ is the coefficient of viscosity. Adapting this to the present case, it becomes

$$\mu = FDR_1(R_1^2 - R_2^2)/8\pi^2 L R_1^2 R_2^2$$

where D is the deflection at a speed of one turn per second, for which ω is 2π, and F is the torsion constant of the wire. The results are:

Outer cylinder, No. 1, $\mu = 0.01020$ dyne.
Outer cylinder, No. 2, $\mu = 0.01010$ dyne.

The lower end of the outer cylinder slipped somewhat loosely into a sleeve which kept it centered at the bottom, while allowing it to be tipped about slightly, and centered at the top by adjustment. In each case a set of observations was made with the top out of center by a measured amount, in order to obtain an approximate value for the error arising from the fact that the outer cylinder was not truly cylindrical. When the two cylinders are set coaxially, the greatest difference between two radii gives δt, the greatest difference in thickness of the liquid layer. At a given point on the surface of the inner cylinder this change in thickness would occur twice in each revolution. When the outer cylinder is tipped so that its upper end is off center, the greatest change in thickness, $\delta_1 t$, occurs but once in each revolution. Assuming that for such small variations, the error is proportional to the first power of the effective δt, the error in the first case would be proportional to $2\delta t$, and in the second to $2\delta t + \delta_1 t/2$. In the table of results, D_1 is the deflection obtained when the outer cylinder was tipped.

	D	D_1	δt	$\delta_1 t$
Outer cylinder No. 1.	1.615	1.595	0.0023 cm.	0.03 cm.
" " " 2.	0.821	0.813	0.0150 cm.	0.05 cm.

This gives the following corrections to be applied to the results:

	Correction.	Corrected μ.
No. 1.	+ 0.3 per cent.	0.01023
" 2.	+ 1.0 " "	0.01020

The thermometer used had not been calibrated, and Professor Ames, of Johns Hopkins University, very kindly arranged to have it compared with a Tonnelot standard thermometer. The comparison, made by Mr. Chas. Waidner, showed that at 20°, the temperature of the above determinations, the thermometer differed from the Paris nitrogen standard by 0°.03, somewhat less than the probable error of a reading. So that no temperature correction is necessary.

To compare with these results, the value of the coefficient from the observations of Poiseuille, computed by the formula previously given, is $\mu = 0.0101$.

RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO, March, 1898.

THE APPLICATION OF THE MANOMETRIC FLAME TO THE TELEPHONE.

BY LOUIS W. AUSTIN.

A CONVENIENT method of showing visually the complex motions of the diaphragm of a telephone receiver seems of some considerable scientific interest. The methods which have been used for studying these vibrations are for the most part complicated and difficult to carry out, and do not any of them, so far as I know, permit the accurate study of vibrations of any degree of complexity.

The great sensibility of the manometric flame to small changes of gas pressure is well known and since the possibility of preserving its records photographically has been shown by Professor Merritt[1] the field of its usefulness has been greatly increased. This great sensibility suggests the possibility of its use in making visible the sound waves produced in the telephone. In order to test the feasibility of this idea a telephone receiver was connected to an ordinary manometric capsule by means of a rubber tube passing through a cork cemented into the opening in the telephone cap. The telephone was then connected in a shunt from the alternating circuit and about .01 ampère sent through it. This made the flame dance excitedly, but when examined in the revolving mirror the image showed very little resemblance to the known form of current wave. The real cause of these inaccuracies was not at first apparent. Several different jets and capsules were used and changes were made in the distance between the telephone diaphragm and the cap, as it was thought that perhaps the diaphragm might come in contact with the cork in the opening, but it was not until the connecting tube was done away with that any improvement was discovered. In the new arrangement a jet was inserted directly through the rubber cork in the telephone cap and another hole drilled in the cap through which the gas was introduced, thus making a manometric capsule of the telephone itself. These changes seemed decidedly beneficial, showing that at least a large part of the difficulty lay in the friction and elasticity of the connecting tube. As it was thought possible that the remaining inaccuracies might be due to pulsations set up in the rubber tube introducing the gas, the gas opening in the cap was constricted to about the size of the opening in the jet. After this change had been made, the lower edge of the luminous part of the flame as seen in the revolving mirror assumed nearly the sine form, and the sensibility of the apparatus was increased in a marked degree. Fig. 1 shows the general arrangement of the telephone in its final form, *A* being the jet passing through the cork *C*, and *B* the inlet for the gas.

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[1] Ernest Merritt, PHYS. REV., Vol. I., pp. 166, 1893.

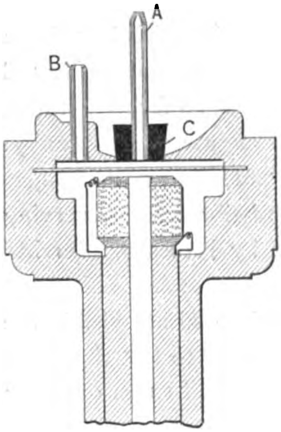

Fig. 1.

The apparatus has been tried with a number of different alternators and the curves from all of these seem to show their known peculiarities of form, though it must be confessed that a certain distortion seems to be present. The reason for this has not been with certainty determined, but it seems probable that it is due at least in part to the flame itself and its tendency to flare.

In these earlier observations drawings of the wave forms were made, but the fleeting character of the images made their reproduction in this way difficult and somewhat uncertain, and it was therefore decided to try photography. As the ordinary illuminating gas does not give a flame which is actinic enough for the purpose unless mixed with oxygen as suggested by Professor Merritt, acetylene was tried. This was found to be highly satisfactory photographically, but the distortion seemed to be increased so that the photographed curves are probably much less accurate than those observed in the revolving mirror when the illuminating gas was used. The photographs were taken with an ordinary camera which was swung around in front of the flame on a kind of whirling table, the camera being placed at such a distance as to make the image not far from the same size as the flame.

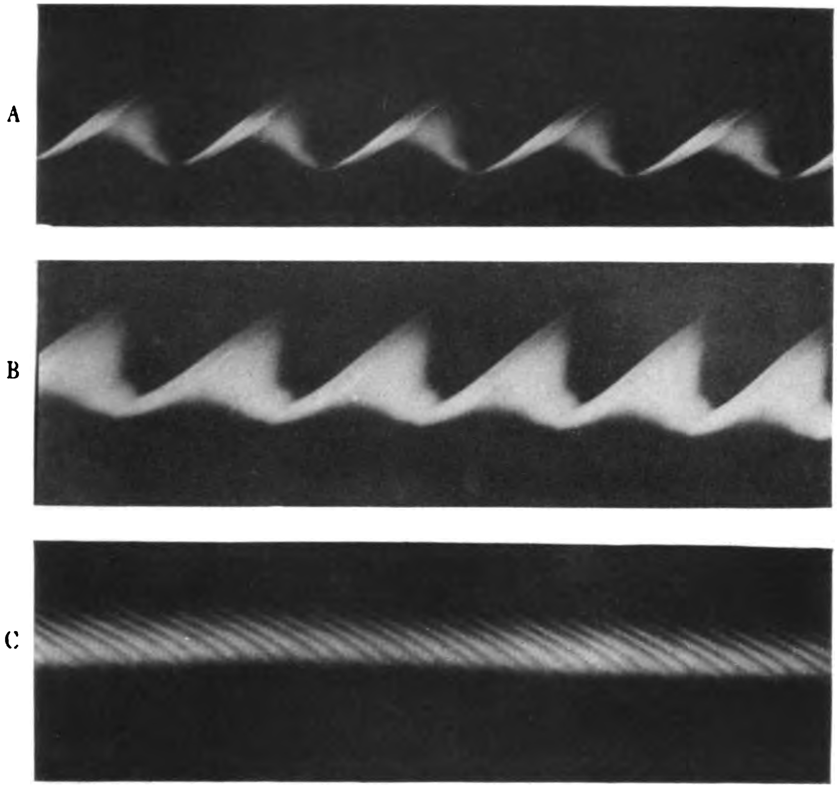

FIG. 2 (AUSTIN)

In Fig. 2, *a*, is shown a photograph of the current curve of the Madison day incandescent lighting system, with a flame about 15 mm. high. The flaring tendencies are here much worse than in the case of the illuminating gas, the left side of each wave being especially distorted from this cause. In *b* the same current curve is shown photographed with a flame 8 mm. high and with a smaller current through the telephone. This seems to be less distorted, but at the same time loses some of the distinctness of its characteristics.

It was found here as well as in the case of the illuminating gas that when a certain amplitude of vibration of the telephone diaphragm was exceeded the flame curve became discontinuous and gave out a loud humming sound reproducing the note of the transformer, this critical amplitude being apparently roughly proportional to the height of the flame.

The wave forms produced by speaking into a carbon transmitter were also observed. It was found that any tone which sounded strong and loud when heard in a receiver produced a well-marked motion in the flame, but as was to be expected the latter did not respond to the weaker sounds. In Fig. 2, *c*, is shown a photograph of the flame when the vowel a, pronounced as in far, was spoken into the transmitter. The flame in this case was about 1 cm. high. It seems probable that the small undulations of the bottom of the flame, which are quite clear with the illuminating gas but unfortunately indistinct in the photograph, represent the real wave form of the sound.

While it had been already shown that the lower line of the luminous part of the flame followed quite accurately the motions of the diaphragm, it was thought worth while to investigate what degree of proportionality existed between the rise in the top of the flame and the potential difference across the terminals of the telephone. To try this the following experiment was carried out: An alternating current of about 0.8 ampère was sent through a bare wire so as to produce a fall of potential of about 0.07 volt per cm. along its length. From this various voltages were applied to the telephone, it being assumed that the motion of the telephone diaphragm could be considered proportional to the difference of potential at its terminals. A millimeter scale was mounted close by the flame and both were observed through a large lens magnifying about three diameters. This enabled readings to be taken to 0.1 mm. with considerable certainty. Observations were made with flames of different heights both in the case of illuminating gas and acetylene. Jets of four different-sized openings were used, 0.28 mm., 0.6 mm., 1.1 mm., 1.8 mm. With illuminating gas it was found that the rise in the top of the flame was, as nearly as could be observed, proportional to the voltage, up to about the point where the buzzing of the flame became quite noticeable. It was also found to be nearly independent of the original height of the flame up to 50 mm. in the case of the two smaller jets. The smallest jet, 0.28 mm., was found to be less than half as sensitive as the others, while the two largest seemed less regular in their action, therefore 0.6 mm. was chosen as the best size for use. With this the rise in the flame was about 6 mm. per volt. The low acetylene flame behaved much the same as the illuminating gas, but the high flame seemed to increase in height more rapidly than the voltage.

During the observation it was noticed that the lower part of the luminous portion of the illuminating gas flame when vibrating appeared to draw itself down in the form of an inverted cup which was very sensitive to slight changes in voltage, moving up and down constantly, apparently at each revolution of the engine.

The above observations suggest several possible lines of usefulness for the manometric telephone.

1. It may be used to show in the lecture room the motions of the telephone diaphragm, and illustrate the undulations of an alternating current.

2. It may, perhaps, be developed so as to offer a practical and convenient method of tracing alternating current curves.

3. In connection with a second manometric flame actuated by a tuning fork of known period it becomes a frequency teller.

4. It may be used in studying the distortions in sounds, produced by telephone transmission.

5. It offers a convenient method of comparing small alternating electromotive forces.

THE UNIVERSITY OF WISCONSIN, Dec., 1900.

MOUNTING FOR TUBE CONTAINING LIQUEFIED CO_2.

By Edwin H. Hall.

In Fig. 1, which shows a vertical section of the apparatus, *L* is a massive leaden base supporting a vertical pillar which carries a strong brass tube *BB*. Each end of this tube is closed by a screw cap, the flat inner surface of which is covered with cork. Perforated plugs of cork, the top one of which is marked *c*, hold the CO_2 tube, *tt*, secure in the upright position. *T* is a thermometer the bulb of which is near the meniscus in *tt*. V_1, supported at any desired height by the arm *A*, is a vessel containing water at, let us say, 27° C. V_1 has communication through the rubber tube *R* and through *BB*, with a similar vessel V_2, containing water near 37° C. The temperature of the water in *BB* is of course intermediate.

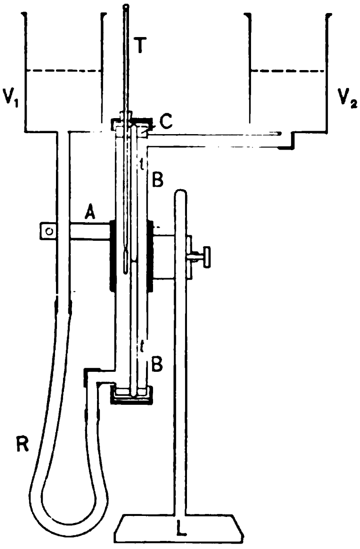

Fig. 1.

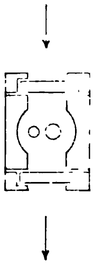

Fig. 2.

In Fig. 2, which shows a horizontal section through the middle of *VB*, the arrows indicate the line of sight, which passes through two thick plates of glass. Each glass plate is held in place by a strong flanged frame of brass, fastened by screws not shown.

As the meniscus moves up and down a centimeter or more, it is well to make the glass windows three or four centimeters long.

To make the meniscus vanish it is only necessary to lower V_1 a few centimeters, whereupon the warmer water, flowing down from V_2 into BV, so heats the tube *tt* that the liquid part of its contents expands considerably and then becomes indistinguishable from the vapor. To restore the meniscus, raise V_1 a few centimeters above the level shown in the figure.

NEW BOOKS.

(1) *Polyphase Electric Currents and Alternate-Current Motors.* (Second, enlarged edition.) By SILVANUS P. THOMPSON. New York, Spon & Chamberlain, 1900.

(2) *Theory and Calculation of Alternating Current Phenomena.* (Third edition, revised and enlarged.) By CHARLES PROTEUS STEINMETZ, with the assistance of ERNST J. BERG. New York, *Electrical World and Engineer*, 1900.

(3) *Standard Polyphase Apparatus and Systems.* (Second edition.) By MAURICE A. OUDIN. Pp. 242. New York, D. Van Nostrand Co., 1900.

These are new editions of three useful books relating to different phases of a common subject. Professor Thompson's book has been revised and exactly doubled in size, the 244 pages of the first edition being expanded to 488 in the second. Some changes are made in the original matter and material has been added on induction motors. Chapters VII. and VIII., on the Graphic Theory of Polyphase Motors, have been developed by Mr. Miles Walker, who, together with Mr. A. C. Eborall, has assisted in the revision of the work. Eight folding plates of scale drawings are included and colored illustrations have been made use of in the text to make clear the diagrams of polyphase windings.

The third edition of Mr. Steinmetz's work has shown less expansion—namely, from 424 pages in the first edition to 512 in the third—but its value has been very much enhanced by a careful revision by which errors have been reduced; certain chapters have been rewritten and the treatment made more systematic as to notation. The thorough overhauling has greatly improved the book. To the thirty chapters in the first edition only two have been added, namely, Chapter XII., "Power and Double Frequency Quantities in General," and XIV., "Symbolic Representation of Alternating Wave," these chapters occupying 28 pages. The chapters on topographical method, on distributed capacity and inductance, and on frequency converters and induction machines have been revised and enlarged; only minor changes being made in the remainder of the book.

The work by Ouden apparently differs from the first edition chiefly in its revision.

These three works encroach but little upon each other. Ouden treats of the material—the apparatus—which forms the subject matter for any theoretical discussion. The writer shows a wide familiarity with his subject, both in theory and in practice, but limits himself exclusively to a discussion of apparatus and systems. Naturally much of this information can be gained from trade publications, but not set forth in so useful a manner. The book contains some careless inaccuracies of expression, not enough however to seriously detract from its worth; it is valuable for one who is studying the theory of alternating currents and desires information concerning the concrete machines to which this theory applies.

Steinmetz's work is a classic and contains a wealth of original material which is rarely approached in any book of its class. For the most part it is abstract, and much study from the reader is required for its mastery. The engineer or student who grasps its methods has acquired indeed a valuable tool.

Thompson's book is written in the same easy style which characterizes his other works; the apparent simplicity often compensates for lack of rigor. It falls between the other two works in style, containing descriptions of apparatus and theory combined. It familiarizes the reader with a subject not treated with equal fullness elsewhere.

F. Bedell.

Ames's Scientific Memoirs, No. 10. The Wave Theory of Light. Memoirs by Huygens, Young & Fresnel, edited by Henry Crew. New York, The American Book Co., 1900. Pp. xv + 164.

This little volume is the first of the well-known series of scientific memoirs begun under the directorship of Professor Ames, and hitherto published by Harper Bros., to be issued by the American Book Co. In it the editor, Professor Crew, has done something more than merely to reproduce and bring together in a convenient form the first three chapters of Huygens's Treatise on Light, Young's three papers (entitled, "Theory of Light and Color, The Production of Colors not Hitherto Described and Experiments and Calculations Relative to Physical Optics") and Fresnel's celebrated memoir on the diffraction of light. He has in a short but exceedingly interesting and suggestive preface pointed out the relation of these works to the earlier investigations of Robert Hooke and to the work of Newton on the one hand and the bearing of the later researches of Fizeau, Foucault, Michelson and Morley, Stokes, Maxwell, Hertz and Zeeman on the other. The three brief biographical sketches which follow the papers of Huygens, Young and Fresnel respectively are good reading and the bibliography with which the volume closes, while by no means complete, offers a useful list of some of the more important transactions and memoirs dealing with undulatory theory of light.

E. L. N.

Volume XII. *March, 1901.* *Number 3.*

THE

PHYSICAL REVIEW.

THE VARIOUS DETERMINATIONS OF THE E.M.F. OF THE CLARK CELL.

By Henry S. Carhart.

LATIMER CLARK in a communication to the Royal Society, May 30, 1872, made some general statements that are now known to be eminently true. He concludes the abstract of his paper as follows:[1] "The standard of electric potential is second only in importance to that of the standard of electric resistance; and the use of such a standard * * * admits of a variety of applications which it is believed will be found of great value in electrical research." It was many years before these statements were generally believed by electricians, but it has now come to be recognized that a good standard cell is of greater importance than a silver voltameter. The electromotive force of the Clark cell is now known with greater precision than the electrochemical equivalent of silver. The recent literature bearing on this constant, and its relation to the value of the mechanical equivalent of heat, render a recapitulation and reduction of its various determinations of considerable interest.

The earliest determination is that of Latimer Clark himself. It has the merit of being an absolute potentiometer method. The two elements of the determination were the measurement of a current and a resistance. The former was made by means of the electrodynamometer constructed for the British Association, or by the use of a sine galvanometer. The potential difference between the terminals of his current-measuring instrument was balanced against the E.M.F. of his standard cell. The resistance entering into the result was that of the electrodynamometer or the sine galvanometer. No current was taken from the standard, and its E.M.F. was equal to the product of the current and the resistance of the instrument.

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[1] Proc. Royal Soc., Vol. 20, p. 444, 1872.

The mean of eighteen trials with the electrodynamometer was 1.45735 at 15.5° C. The mean of thirteen with the sine galvanometer was 1.45621 at the same temperature. The final mean value was then 1.45678 at 15.5° C., or as given by Clark, 1.457 British Association units. But one B. A. unit equals 0.9866 international ohm. Therefore Clark's value reduced to present units at 15° is 1.4378.

So far as ascertained the next determination of the E.M.F. of the Clark cell was made by the writer in January, 1882, in Berlin.[1] The measurement was incidental to another investigation and was confined to a single cell belonging to the Physical Laboratory of the university. The method was the now well-known one of the silver voltameter. It is substantially the same as that employed by Clark, with the silver voltameter substituted for the electrodynamometer. The fall of potential over a known resistance was balanced against the E.M.F. of the standard cell. The results were not published till after Lord Rayleigh had made his determination of the electrochemical equivalent of silver in 1884. The published value was 1.434, but no corrections were made to reduce the E.M.F. to 15°, and the ratio of the Siemens unit of resistance to the ohm was taken to be $\frac{100}{106}$. It is perhaps worth while to make these corrections now when the requisite coefficients are well known. The following are the data :

Trial.	Temp. of Cell.	Res. in S. U.	Temp. of Res.	Silver Dep. per min.
1	18°	20	19°	0.0051 gm.
2	17	20	19	0.0051 "

$$\text{The current } I = \frac{0.0051}{0.001118 \times 60} = 0.07603 \text{ ampère.}$$

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[1] Amer. Jour. Sci., Vol. XXXVIII., Nov., 1884.

The resistance box was correct at 20°. With a temperature coefficient of 0.0004 for German silver, 20 Siemens units equal 19.992 at 19°, and 19.992 × 100/106.3 = 18.807 ohms. Then

$$E = IR = 0.07603 \times 18.807 = 1.4299 \text{ volts.}$$

But the cell was at a temperature of 18° in the first trial and 17° in the second. The formula now used for temperature corrections of the Clark cell at the Reichsanstalt is

$$E_t = E_{15} - 119 \times 10^{-5}(t - 15) - 7 \times 10^{-6}(t - 15)^2.$$

This formula gives for the correction in the first case 0.0036, and in the second case, 0.0024. We have therefore

Trial 1 . . . . . . 1.4299 + 0.0036 = 1.4335
Trial 2 . . . . . . 1.4299 + 0.0024 = 1.4323
Mean at 15° 1.4329

No great weight is to be attached to this determination because the resistance used was not standardized, nor is it certain that its temperature was exactly indicated by the thermometer. The Clark cell was a large one containing a thermometer with its bulb within the contents of the cell. The balance with the silver voltameter was carefully maintained, the weighings were made after careful drying, and the deposit was washed in such a way as to avoid loss.

The next determination is that of Lord Rayleigh in 1884.[1] The method employed was a modified potentiometer method, the current being measured by the current balance which Lord Rayleigh used in his research on the electrochemical equivalent of silver. The value which Lord Rayleigh derived from all his determinations was 1.454 B. A. units at 15°. To reduce to volts the correction factor expressing the B. A. unit in terms of the ohm was introduced. The factor used by Lord Rayleigh was one B.A. unit equals 0.9867 ohm, giving the E.M.F. of the Clark cell 1.435 volts at 15°. If we employ the factor 0.9866 adopted by the British Board of Trade to convert B. A. units into ohms or volts, then Lord Rayleigh's value for the Clark cell is 1.4345 volts at 15°.

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[1] Phil. Trans. Royal Soc., Part II., 1884.

Another determination with the silver voltameter is that of A. v. Ettinghausen.[1] He assumed Kohlrausch's second value for the silver equivalent, 0.0011183, and found for the E.M.F. of the Clark cell at 15.5°, 1.433 volts. If we correct for the electrochemical equivalent, 0.001118 instead of 0.0011183, and reduce to 15°, we have 1.434 volts.

A very elaborate investigation of the Clark cell was made by Glazebrook and Skinner in 1891–92.[2] The current was measured by the silver voltameter. Great precautions were taken to keep the standard resistance at a constant temperature. The mean of nine determinations was 1.4342 volts at 15°. To reduce to 15° the authors of the paper used the coefficient—0.00077. This gives a slightly smaller correction than the Reichsanstalt formula. Since the cell was always above 15°, the corrections are positive; the mean difference is two units in the fourth decimal place. Reduced to a common temperature coefficient, the final result of Glazebrook and Skinner's investigation is 1.4344 volts.

This is almost identical with the value derived from Lord Rayleigh's paper. He used for temperature corrections the coefficient —0.00082, which is equivalent to that of the Reichsanstalt formula for small ranges of temperature.

A good deal of interest attaches to the work done at the Reichsanstalt on Clark and Cadmium cells, and great confidence is felt everywhere in the results attained. In 1896 Kahle made an absolute measurement of the E.M.F. of the H-form of Clark cell by means of the Helmholtz absolute electrodynamometer.[3] This very elaborate instrument is fully described in Kahle's paper which is published as a contribution from the Reichsanstalt. For the E.M.F. at 0° C. he found 1.4488 volts. A direct comparison for the Clark at 0° minus the Clark at 15° gave $E_0 - E_{15} = 0.0166$. Hence at 15° the E.M.F. of the Clark cell found by Kahle is 1.4322 volts. The volt here corresponds to the international ohm, but not to the volt a sdefined in the legal definition of the Clark cell. The above value for the Clark cell has not been used by the Reichsanstalt.

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[1] Zeitschrift für Elektrotechnik, 1884, XVI. Heft.

[2] Phil. Trans. Royal Soc., Vol. 183 A, 1892.

[3] Wied. Annal., Vol. 59, 1896, p. 573.

For about four years the Reichsanstalt has employed the following values:

Clark cell: 1.4328 int. volts at 15° C.
Cadmium cell: 1.0186 int. volts at 20° C.

The cadmium cell is the same as the Weston except that the $CdSO_4$ solution contains an excess of crystals, while the Weston is made with a solution saturated at 4° C. The manner in which the value 1.4328 for the Clark cell was obtained may be gathered from a paper by Jaeger and Kahle on "Mercury-Zinc and Mercury-Cadmium Elements as Standards of Electromotive Force." [1]

Three series of measurements were made with a large number of cells to determine the two ratios,

$$\frac{\text{Clark } 15^\circ}{\text{Cadmium } 20^\circ} \text{ and } \frac{\text{Clark } 0^\circ}{\text{Cadmium } 20^\circ}.$$

The results for the three series are shown in the table:

Date.	$\frac{\text{Clark } 0^\circ}{\text{Cadm. } 20^\circ}$	$\frac{\text{Clark } 15^\circ}{\text{Cadm. } 20^\circ}$	Clark 0° — Clark 15°
March, 1896	1.4227	1.4066	0.0164
Jan., 1897	1.42277	1.40676	0.01631
Nov., 1897	1.42280	1.40660	0.01650
Means	1.42277	1.40663	0.01642

The last column is easily obtained from the preceding two. The next step in fixing the E.M.F. of the Clark cell is Kahle's long series of determinations with the silver voltameter.[2] Assuming 0.001118 as the silver equivalent, he obtained for the Clark at 0° 1.44945, and for the cadmium at 20°, 1.01849. The ratio of these two numbers is 1.42313, or 0.00036 greater than the result of the direct comparison. Since the ratio of the silver voltameter measurements is affected by a greater uncertainty than the one directly observed, the difference is divided between the two electromotive forces obtained by the silver voltameter in proportion to their magnitudes. The value for the Clark at 0° is thus reduced to 1.44923. Subtracting the fall of E.M.F. between 0° and 15°, and we have Clark at 15° equals 1.4328 volts.

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[1] Wied. Annal., Vol. 65, 1898, p. 926.
[2] Wied. Annal., Vol. 67, 1898, p. 1.

Similarly the Cadmium cell becomes 1.0186 at 20°. While this method is something of an improvement on the old one with the silver voltameter, it is yet fundamentally the same and leaves much to be desired.

A year ago Professor Lindeck and myself made several series of observations at the Reichsanstalt to redetermine the ratios between the Clark at 0° and at 15° and the cadmium at 20°. A large number of cells, new and old, were used. The precautions taken to maintain a constant temperature during a series of observations proved highly satisfactory. The comparisons were made rapidly by means of the well-known compensating apparatus devised at the Reichsanstalt and made by Wolff in Berlin. Three series of comparisons gave as a mean for the ratio Clark 15°/Cadmium 20°, 1.40679.[1]

Nine Clark cells were then placed in a petroleum bath and completely surrounded by pounded ice for five days. Eight series of comparisons gave, Clark 0°/Cadmium 20° = 1.42283.

These new ratios of the Clark at 0° and at 15° compared with the Cadmium at 20° give, Clark 0° − Clark 15° = 0.01634. Then by the method of reduction used by Dr. Kahle, 1.44929 − 0.01634 = 1.43295 at 15°.

The above new ratios are published in the last "Thätigkeitsbericht" of the Reichsanstalt, but the recommendation is made that the old value for the E.M.F. of the Clark cell at 15°, viz., 1.4328 should be retained. This recommendation does not appear to be quite reasonable, since the new ratios are derived from more concordant series of observations than the old ones, and their application to Kahle's results from the silver voltameter deposits gives a value very near 1.433 volts at 15°.

During the summer of 1899 an absolute determination of the E.M.F. of the Clark cell at 15° was made by myself and Dr. Guthe. The fall of potential over a known resistance was compared by a potentiometer method with the E.M.F. of two Clark cells of the modified H-form joined in series.[1] The current was measured by our absolute electrodynamometer of simple construction.[2] The resistance was determined in terms of two one-ohm coils with Richsanstalt certificates. The result of three determinations was E.M.F. of Clark at 15° is 1.4333 volts.

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[1] Zeitschrift für Instrumentenkunde, June, 1900, p. 176.

This value we do not consider final. The measurement may be made under improved conditions, and the suspended coil wound on a hard rubber cylinder was probably not exactly circular in section. A new porcelain cylinder with a guaranteed external diameter has been obtained from the Royal Porcelain Works in Berlin through the courtesy of Mr. Louis J. Magee, of that city. It has not yet been mounted in the electrodynamometer. A large porcelain cylinder will also be tried for the fixed coil.

Finally an interesting side light has been thrown on the value of the E.M.F. of the Clark cell by the fact that Griffiths' determination of the mechanical equivalent of heat by an electrical method gave a result larger than Rowland's by a constant small amount of one part in 400 or 500. Since the E.M.F. enters the result as the square, an error in the E.M.F. of the Clark cell of about one part in 1,000 would explain the discrepancy. This would mean a value of a little less than 1.433 instead of 1.434.

In a recent communication to the Royal Society on a new determination of the mechanical equivalent of heat by an electrical method differing from that of Griffiths, Barnes, of McGill University,[3] points out that his result is higher than those obtained by direct mechanical methods. He attributes the discrepancy to an incorrectness in the assumed value of the E.M.F. of the Clark cell. A value of 1.43325 instead of 1.4342 volts causes the discrepancy to disappear.

In the light of such facts it is interesting to place before us a tabular view of the several determinations which I have briefly described, and which I have reduced to common terms:

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[1] Phys. Rev., Vol. IX., No. 5, 1899, p. 288.

[2] Phys. Rev., Vol. VII., No. 39, 1898.

[3] London Electrician, Oct. 19, 1900.

Observer.	Date.	Method.	Result.
Clark.	1872	Absolute.	1.4378
Carhart.	1882	Silver Voltam.	1.4329
Rayleigh.	1884	Absolute.	1.4345
Ettinghausen.	1884	Silver Voltam.	1.434
Glazebrook & Skinner.	1892	" "	1.4344
Kahle.	1896	Absolute.	1.4322
Jaeger & Kahle.	1898	Silver Voltam.	1.4328
	1899	" "	1.4329
Carhart & Guthe.	1899	Absolute.	1.4333

If we omit Clark's determination, because his cells set up with boiled zinc and mercurous sulphates are not comparable with the others, only three absolute determinations have been made. The mean of these is 1.4333 volts at 15°.

A study of the above table can hardly fail to produce the conviction that the E.M.F. of the Clark cell at 15° C. is nearer 1.433 than 1.434 volts.

UNIVERSITY OF MICHIGAN, Dec. 1, 1900.

VELOCITY OF IONS DRAWN FROM THE ELECTRIC ARC.

By C. D. Child.

THERE appeared in a recent number of the Physical Review[1] an article by the present writer offering an explanation of the electric arc on the assumption that the current in the arc is carried by ions. In order to account for the fall of potential through the arc it was necessary to assume in that explanation that the positive ions move more rapidly than the negative under similar conditions. There appeared to be some difficulty in such an assumption, since in all cases which had been studied the negative ions had been found to move the more rapidly.

Method here used.—Since the publication of that article a method of investigating the arc further has been tried. The method is a modification of one suggested by Prof. J. J. Thomson[2] and its application to the study of the velocity of ions drawn from a flame has already been published.[3] In that article it was shown that in the case of a very large supply of ions of both kinds a comparison of the velocities of the negative and positive ions could be made by simply comparing the positive and negative rates of discharge from the source of ionization to bodies near it. If the discharge takes place from one regular surface to a second regular surface, it is possible to find the exact values of the velocities. The arc, however, is not susceptible of analytical treatment. Moreover in this case the chief point of interest is to prove that the positive ions move the more rapidly and it is of secondary interest to show exactly what that velocity is.

The conclusion of the discussion previously given may be stated as follows. Let Fig. 1 indicate the cross section of two surfaces.

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[1] Phys. Rev., 10, p. 151.

[2] Phil. Mag. (5), 47, p. 265.

[3] Phys. Rev., 12, p. 65.

Let there be in *A* a supply of both positive and negative ions. If the other surface *B* is charged positively, negative ions will be drawn toward *B*. If *B* is negative, positive ions will be thus drawn. If the supply of ions of both sorts in *A* is very large as compared with number drawn out, the current carried by the positive ions will be larger, if the positive ions move the more rapidly; that carried by the negative, if the negative ions move the more rapidly. This will also be true whether the surfaces *A* and *B* are regular or irregular.

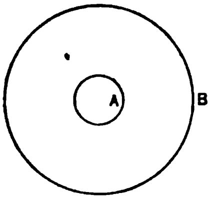

Fig. 1.

The instruments used and the methods of measuring the rates of discharge were the same as those described in the article on the velocity of ions drawn from a flame.

There was an added difficulty in this case due to the fact that the potential of the arc could not be made very much different from that of the ground. The arc was supplied with current from a storage battery of thirty cells. This battery and its connections were insulated as far as possible, but the fumes from the acid made the insulation poor. When the attempt was made to raise the potential of the arc above that of the ground the water battery used for the purpose became quickly polarized. Consequently the arc was kept at near the potential of the ground and the metal to which the discharge took place was charged, the water battery being between the charged metal and the electrometer or galvanometer. In this way the instrument used to measure the rate of discharge was always near zero potential.

The current flowing from the arc to the metal will be called the positive current. This current is carried by positive ions. The current in the opposite direction is carried by negative ions and is called the negative current. The radius of *B*, Fig. 1, will be indicated by b and the difference of potential between *A* and *B* by V_b.

In the first experiments a small piece of sheet iron 1 cm. square was placed 1 cm. from the arc, and the current to this from the arc was measured by a galvanometer. It was found that the movements of the arc produced great changes in the rate of discharge from it. The positive current appeared to be the greater, but one could not be absolutely certain. To test this a reversing key was placed in the circuit and so operated by a pendulum that the potential of the charged plate was reversed once in .7 sec. Since the period of the galvanometer was 12.6 sec. for a complete swing, the needle did not move far from its mean position, when the potential of the charged metal was constantly reversed. By this means it was possible to determine the difference between the two currents.

Since the reversing key might send the current longer in one direction than in the other, the current was occasionally reversed before it was brought to the key described above, and the arrangement was so adjusted that this occasional reversal had no effect on the reading.

In the first trial a small carbon connected to ground was placed in the arc, and it was then assumed that the protential of the arc was zero. As near as could be estimated the average positive current was 3.1×10^{-8} ampère, the negative 1.8×10^{-8} ampère. The difference as shown by the reversing key 1.3×10^{-8} ampère.

In other experiments where a cylinder was placed about the arc the fluctuations of the arc had less effect on the rate of discharge and in most cases this reversing key was not needed.

Lest some error was being made in the sign of the current, the arc was replaced by the flame from a Bunsen burner. It has already been shown that with this the negative current is the greater, so that with the flame the current should be greater in one direction and with the arc in the other. On testing it this was found to be the case.

The Potential of the Arc Varied.—There was in this the possibility of error, since the potential of the arc was assumed to be the same as that of the small carbon inserted in it. One might think that possibly the arc did not assume the potential of the carbon, or that the discharge came from one of the carbons of the arc. To make sure that no error was being introduced in this way the rate of discharge was noted when different parts of the arc were grounded, or, what amounted to the same thing, when different points on a shunt placed about the arc were grounded. And instead of placing a small piece of iron near the arc a cylinder 2 cm. long and 4.5 cm. in diameter was used. This cylinder was made of tin. The arc was placed in the center of this as nearly as possible. Above and below this, but insulated from it were cylinders of the same diameter. These were kept at the same potential as the central cylinder and served the same purpose as an ordinary guard ring. The arc and cylinders were vertical. The difference of potential between the ring and the ground was 95 volts.

With the ground at the negative carbon the negative current was 1.1×10^{-8} ampère, and the positive 1.2×10^{-8}.

With the ground ¼ of the way from the negative to the positive carbon the negative current was $.9 \times 10^{-8}$ ampère, the positive 1.3×10^{-8}.

With the ground half way between the positive and negative carbon the negative current was $.85 \times 10^{-8}$ ampère, the positive 1.5×10^{-8}.

With the ground ¾ of the way to the positive carbon, the negative current was $.8 \times 10^{-8}$ ampère and the positive 1.7×10^{-8}.

With the ground at the positive carbon the negative current was $.6 \times 10^{-8}$ ampère, the positive 1.9×10^{-8}.

It is seen that in every case the positive current was the greater. According to Mrs. Ayrton[1] the difference of potential between the negative carbon and the arc is about ¼ of the difference of potential between the two carbons, so that the arc will be practically at zero when the ground on the shunt is ¼ of the way from the negative to the positive carbon. In the rest of the work the ground was kept at that point.

Position of the Arc Varied.—During this experiment the arc had been on the level with the center of the cylinder to which the discharge was taking place. The position of the arc was then raised 1.5 cm. The lower carbon was negative and was nearer to the cylinder. It was found that in this position the currents were much smaller but that the ratio between the two currents was practically the same as before. The positive current was 4.4×10^{-9} ampère, the negative 2.2×10^{-9}.

The current through the arc was then reversed so that the cylinder was nearer the positive carbon, and the currents were practically the same as before this reversal. This would indicate that the discharge was from the arc itself and not from either of the carbons, or at least was not from one carbon more than from the other.

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[1] Lond. Elec., 41, p. 720.

Potential of Vapor from Arc Studied.—It has been stated by some observers[1] that the vapors from the arc are charged and it was thought that this might be affecting the results here given. A cylinder 5 cm. long and 4.6 cm. in diameter was accordingly placed about the arc and the potential which this assumed when insulated was noted. The potential of the arc was also determined roughly by means of a small carbon placed in the arc. The potential of the arc has been studied thoroughly by Mrs. Ayrton, so that no attempt was made to do more than to show that the behavior of the arc here used was normal.

The potential was found by grounding different points on the shunt about the arc until a point was found which caused the small carbon to assume zero potential. The potential of the arc fluctuated through a few volts, but the average potential was practically the same which others have found. The potential of the cylinder about the arc was found in the same way, and was found to be somewhat different from that of the arc.

To test this further one pair of quadrants of the electrometer was connected to the cylinder about the arc and the other pair to the small carbon placed in the arc. It was then found that the cylinder assumed a potential between that of the small carbon and that of the upper carbon of the arc. Thus if the upper carbon was positive the cylinder was positive as compared with the small carbon, the difference being about 14.5 volts. If the upper carbon was negative the cylinder was negative, the difference being 7 volts. The difference of potential between the small carbon and positive terminal was 23 volts and that between the small carbon and the negative terminal 9 volts.

The potential of the cylinder about the arc was also examined when salts were placed in the arc and when tin was placed in one of the carbons which had been hollowed out, and in every case the cylinder was found to have a potential between that of the arc and that of the upper carbon of the arc.

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[1] Wied. Ann., 40, p. 332.

This effect is very similar to that found by Merritt and Stewart[1] except that in their case the potential of the vapor drawn from the arc had the same sign as the lower carbon of the arc. The cases, however, are sufficiently different to account for the different results. As shown bv Merritt and Stewart with their apparatus the arc was enclosed and convection currents carried the vapors from the arc down by the side of the enclosure and up again past the lower carbon and were drawn off into the space where they were examined, so that the lower carbon might easily give its potential to the vapor. In the case here described there was no chance for the ionized vapors to be carried down and receive the potential of lower carbon. They were carried up past the upper carbon and out into the room, so that they had the potential of the upper carbon.

However, this evidently has no bearing on the matter in hand. This effect may be reversed by reversing the current in the arc while the rate of discharge to a charged ring about the arc is independent of the direction of the current in the arc.

Effect not Due to Ultra-violet Light.—The possibility suggested itself that the rate of discharge from the arc was being modified by the ultra-violet light of the arc. This seemed highly improbable since the cylinders surrounding the arc were of tin, but to make sure concerning it a cylinder of wire gauze 9 cm. long and 4.5 cm. in diameter was placed about the arc. This screened off about one-half of the light. About this a cylinder 6 cm. in diameter and 2 cm. wide was placed. The inner cylinder was charged to 100 volts, the outer one was connected to the electrometer. A small charge passed to the outer ring whether the inner cylinder was charged positively or negatively, but scarcely $\frac{1}{100}$ of the amount necessary to account for the difference between the positive and negative discharge which has been noted.

But it was possible to show even more clearly that the effect was not due to ultra-violet light. A small cylinder 4.5 cm. in diameter and 6 cm. wide was placed about the arc and grounded. About this a larger cylinder 6 cm. in diameter and 2 cm. wide was so placed that it was entirely screened from the light of the arc, so that light could not in any way affect the discharge taking place from it. This outer ring was charged and it was found that discharge still occurred and that when the cylinder was charged negatively the rate of discharge was greater than when it was charged positively. This discharge is no doubt due to the fact that some of the lines of force from the outer cylinder bend around the edges of the inner one and draw out ions from the neighborhood of the arc. In this case as in others the discharge produced by the positive ions is the greater.

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[1] PHYS. REV., 7, p. 141.

If there is here any such effect as Lenard[1] has recently described, it would not explain the fact that the current is greater in one direction than in the other.

Current in the Arc Varied.—The effect of varying the current in the arc was then tried and the results are given in the following table. The arc was here surrounded by a cylinder 4.5 cm. in diameter and 2 cm. wide, with guard cylinders on each side. V_b was 95 volts.

Table I.

1 Current in Arc.	2 Positive Discharge.	3 Negative Discharge.	4 Ratio of 2 to 3.
4.5	1.76×10^{-8}	$.83\times10^{-8}$	2.1
6.5	2.28 "	1.16 "	1.96
8.5	2.4 "	1.25 "	1.92

Column 1 gives the current through the arc in ampères. Column 2 the rate of discharge in ampères when the surrounding cylinder was negative, column 3 when it charged positively, and column 4 the ratio between these two values.

In general the rate of discharge becomes greater as the current in the arc is increased, but in all cases the discharge carried by positive ions is the greater, and the variation in the ratio between two rates of discharge is such as might easily be caused by the fluctuations of the arc. In the following experiments the current in the arc was kept as near 5 ampères as was practical:

Diameter of Cylinders Varied.—Cylinders with different diameters were then used and the results are given in Table 2. The cylinders were 2 cm. in width and in each case guard cylinders were placed above and below them. V_b was 95 volts.

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[1] Drude Ann., 1, p. 486.

TABLE II.

1 b	2 Positive Discharge.	3 Negative Discharge.	4 Ratio of 2 to 3.
2.25	17.6×10^{-9}	8.32×10^{-9}	2.1
3.1	4.63 "	2.03 "	2.28
4.5	1.06 "	.59 "	1.8
6.3	.307 "	.17 "	1.8
9.	.122 "	.061 "	2.

Column 1 gives the radius of the surrounding cylinder. The other columns are the same as in the previous table. The variations in the ratios between the two currents are probably due entirely to fluctuations in the current of the arc.

V_b Varied.—Table 3 gives the values of the currents for different values of V_b. In this case b was 2.3 cm. and the width of the cylinder was 2 cm. Column 1 gives the value of V_b. The other columns are the same as in the previous tables.

TABLE III.

1 V_b	2 Positive Discharge.	3 Negative Discharge.	4 Ratio of 2 to 3.
50	4.4×10^{-9}	2.2×10^{-9}	2.
95	17.6 "	8.37 "	2.1
175	52.8 "	24.2 "	2.18
251	88. "	44. "	2.

Theory of Discharge between Cylinders.—Thus far we have only found the comparative velocities of the positive and negative ions. It will be of interest to find even the approximate values in absolute units. If we could treat of the arc as a cylinder of infinite length surrounded by a second such cylinder, the problem could be solved mathematically; or if it were a sphere surrounded by a second sphere with the potential varying according to the same law in all directions, the problem could be solved. But it is neither of these. The arc itself might be treated as a sphere, but the presence of the carbons causes the potential to vary quite differently in different directions. It is, however, of some interest to compute the velocity on the assumption that one or the other of the above cases applies, and the following is a treatment of the case on the assumption that the arc is an infinite cylinder. To do so is not quite as unreasonable as might at first sight appear, since we have only used a small part of the outer cylinder opposite the arc.

The mathematical treatment is similar to that given by Professor Thomson[1] for the case of discharge between plates. Let the space within A, Fig. 1, by supplied with both positive and negative ions and let ions of one sign only be drawn from A to the cylinder B. Let B be charged negatively. Then the ions in this space will be charged positively. Let V be the value of the potential at any point, e the charge carried by each ion, n_1, the number of positive ions per unit volume, k_1, the velocity of the positive ions for unit potential gradient, r, the distance from the center of the cylinders, i, the current through unit area and we have

$$\frac{d^2V}{dr^2} + \frac{1}{r}\frac{dV}{dr} = -4\pi n_1 e$$

and

$$k_1 n_1 e \frac{dV}{dr} = -i_1 = -\frac{I_1}{r}$$

where I_1 is the value of i_1 when $r = 1$.

Or

$$\frac{dV}{dr}\frac{dV^2}{dr^2} + \frac{1}{r}\left(\frac{dV}{dr}\right)^2 = \frac{4\pi I_1}{k_1 r}.$$

Integrating this expression we have

$$\frac{dV}{dr} = -\sqrt{a + \frac{C^2}{r^2}} \quad \text{where} \quad a = \frac{4\pi I_1}{k_1}.$$

By a course of reasoning similar to that given in the PHYSICAL REVIEW, 12, p. 65, it can be shown that $\frac{dV}{dr}$ is very small at the surface of A. Let r_0 be the radius of this cylinder and assume that $\frac{dV}{dr} = 0$ when $r = r_0$, and the above equation becomes

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[1] Phil. Mag., (5), 47, p. 265.

$$\frac{dV}{dr} = -\sqrt{a}\sqrt{1 - \frac{r_0^2}{r^2}}.$$

If this be integrated we have

$$V = -\sqrt{a}\left\{\sqrt{r^2 - r_0^2} + r_0 \sin^{-1}\left(\frac{r_0}{r}\right)\right\} + C'.$$

If $V = 0$ when $r = r_0$,

$$C' = \frac{r_0 \pi \sqrt{a}}{2}$$

and

$$V = -\sqrt{a}\left\{\sqrt{r^2 - r_0^2} + r_0\left[\sin^{-1}\left(\frac{r_0}{r}\right) - \frac{\pi}{2}\right]\right\}.$$

If higher powers of $\frac{r_0}{r}$ may be omitted

$$V = r\sqrt{a}\left\{1 + \frac{1}{2}\frac{r_0^2}{r^2} + \cdots - \frac{\pi}{2}\frac{r_0}{r}\right\}.$$

Substituting the value of a, letting b be the value of r, and V_b the corresponding value of V, solving for k_1 we have

$$k_1 = \frac{4\pi I_1 b^2\left\{1 + \frac{1}{2}\frac{r_0^2}{b^2} + \cdots - \frac{\pi}{2}\frac{r_0}{b}\right\}^2}{V_b^2}.$$

Or in the practical system of units

$$k_1 = \frac{36\pi \times 10^{11} I_1 b^2\left\{1 + \frac{1}{2}\frac{r_0^2}{b^2} + \cdots - \frac{\pi}{2}\frac{r_0}{b}\right\}^2}{V_b^2}.$$

If k_2 is the velocity of the negative ions for unit potential gradient, a corresponding expression for k_2 may be found.

Values Found for k_1 and k_2.—Using the data in Table II. and remembering that the total current to the cylinder is 2π times the width of the cylinder times I, we find that when b is 2.25 cm. and V_b 95 volts the theory gives us 4.1 cm. per volt per cm. for k_1, and 1.95 cm. for k_2. As b becomes larger the values of k_1 and k_2 become smaller. For example when b is 4.5 cm. k_1 is 1.47 cm., and k_2 .82 cm. This corresponds to the similar case with ions drawn from a flame and is what might naturally be expected. The values here found, however, are somewhat smaller than the corresponding values of the ions from a flame. If there were any difference, one would expect the ions from the flame to move with smaller velocity, since the arc is hotter. But the assumption made in deriving the formula given above is too far from the truth to make the numerical results of much importance. It is scarcely worth while to compare the values found for different distances with one another or with the corresponding values for the ions from a flame.

Agreement of Observations with Theory. According to the theory the current should vary inversely as the cube of the radius of the surrounding cylinder. Since the area of the cylinder itself varies as the radius the total current received should vary inversely as the square of the radius. This agrees fairly well with observed data. The current, however, decreases somewhat more rapidly than it should. This may be due either to the fact that the actual conditions do not correspond closely to the assumed conditions, or possibly to a slower motion of the ions as they move further from the arc.

The current should also vary as the square of V_b. It does not, however, vary as rapidly as this, probably again because of the lack of agreement between the assumed and the actual conditions. The increase in the rate of discharge when the current in the arc is increased can be explained by the increase in r_0, the radius of the arc itself, or on the assumption that the velocity of the ions becomes greater as the arc becomes hotter. Further work will be necessary before a full explanation of what has been observed can be given.

Vapors Rising from the Arc.—Thus far the ions have been drawn directly from the arc. One of the experiments performed by Merritt and Stewart[1] indicated that in the vapors rising from the arc the negative ions move the more rapidly. It seemed well to make some further test of this and the following was tried. The arc was placed in a horizontal position and above it was placed a sheet of tin which was connected to the ground. In this there was an opening 1 cm. in diameter directly above the arc. In the vapors carried up through this by convection currents there was a copper wire and about this a cylinder 4.5 cm. in diameter and 2 cm. long. We here again have conditions similar to those indicated in Fig. 1, *i. e.*, a space filled with ions of both signs and about this a space filled with ions of one sign only. We have not so great a supply of ions as in the arc, and yet may reasonably suppose that there were many more in the rising vapor than were drawn out to the surrounding cylinder.

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[1] Phys. Rev., 7, p. 143.

Under these conditions the rate of discharge was found to be greater when the surrounding cylinder was charged positively. No explanation for this has suggested itself other than that this greater discharge was caused by the more rapid motion of the negative ions. This agrees with the conclusion of Merritt and Stewart, although it was scarcely what was to be expected from the work on the arc itself.

It would seem as if of the ions drawn directly from the arc the positive ones move the more rapidly, but that these quickly lose this rapidity of motion and come to move slower than the negative ones. It would be of interest to investigate the change from the condition where the positive ions move the more rapidly to that where the negative ions do, but the present writer has not yet been able to do this.

Arc Between Metals.—Lecher[1] observed in 1888 that the fall of potential at the positive terminal of an arc established between metals was no greater than that at the negative terminal. My own observations indicate that the fall of potential at the positive terminal is slightly less than the other. If this be so, in order to explain it on the hypothesis that the current is carried by ions it is necessary to assume that in such cases the negative ions move the more rapidly. This fact affords a test for the theory. The rates of discharge from the arc between metals was accordingly examined and in every case it was found that when the cylinder surrounding the arc was charged positively the rate of discharge from it was greater than when it was charged negatively indicating that the negative ions here move the more rapidly.

The data found in this work are given in Table IV. Column 1 gives the metal used. Column 2 the rate of discharge when the surrounding cylinder was charged negatively. Column 3 when charged positively. Column 4 the fall of potential at positive terminal in volts. Column 5 that at the negative, V_b was 94 volts b was 2.25 cm. and the width of the cylinder 2 cm. The ground in using the metals was at the middle point of the shunt about the arc. The current through the arc was about 6 ampères.

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[1] Wied. Ann., 33, p. 609.

TABLE IV.

1 Name of Metal.	2 Positive Current.	3 Negative Current.	4 Fall of Potential at the + terminal.	5 Fall of Potential at the − terminal.
Zinc.	$.88 \times 10^{-8}$	1.32×10^{-8}	12	14
Iron.	2.2 "	2.64 "	13	15
Copper.	2.2 "	3.08 "	11	14
Carbon.	1.76 "	.83 "	23	9

Salts in the Arc.—Experiments were also performed with carbons hollowed out and filled with salts. The salts, however, soon evaporated so that the condition of the arc was continually varying and made quantitative measurements impossible. Na_2CO_3 and $CuSO_4$ were tried and when the arc was first started it behaved in respect to the potential of the arc and to the rate of discharge to the surrounding cylinder as an arc between metals, but in a few seconds it changed over to the condition of the ordinary arc in both these respects. This indicates that at first, when the vapor of the salt was abundant in the arc, the negative ions moved the more rapidly, and that when this vapor became less abundant the positive ions moved the more rapidly.

Oxy-hydrogen Flame.—An oxy-hydrogen flame playing on a piece of carbon connected to the ground was put in the place of the arc. When the flame was as hot as it could be made the results were the same as with the arc between carbons. When the flame was not so hot, or when there was no carbon in the flame, but the flame was grounded by grounding the burner, the effect was the same as with a Bunsen burner. The positive current for $b = 4.5$ cm., width of cylinder $= 2$ cm. and $V_b = 95$ volts was 3.1×10^{-8} ampère, the negative 2.8×10^{-8} ampère.

Pencils of iron, copper, zinc, aluminum and platinum were placed in the flame, but in no case was the effect the same as that observed with the carbon. This proves but little, however, since in all these cases the metals melted before observations of value could be taken, and long before they reached the temperature which the carbon assumed.

Summary.—The preceding work may be summarized as follows :

A study of the rate of discharge from an arc to a neighboring body shows that under varying conditions of difference of potential distance and current in the arc itself the positive ions drawn out from the arc move more rapidly than the negative ones. This is not to be explained as an effect due to ultra-violet light or any phenomena previously studied.

The positive ions from a carbon placed in an oxy-hydrogen flame also move the more rapidly. In cases of an arc between metals the negative ions move the more rapidly.

While this work does not prove that the positive ions in the arc itself move more rapidly than the negative ones there, it is in every respect consistent with such a hypothesis, and it shows that it is possible for the positive ions to do so. The question why the positive ions here show this peculiarity is, of course, entirely unanswered. In all the cases so far studied we have carbon and also a very high temperature. It would at present be useless to speculate as to whether this phenomenon is to be ascribed to one or the other of these facts or to some one entirely different. The author hopes in time to publish further experiments bearing on this point.

COLGATE UNIVERSITY, January 25, 1901.

A SPECTROPHOTOMETRIC STUDY OF THE HYDROLYSIS OF DILUTE FERRIC CHLORIDE SOLUTIONS.

By B. E. Moore.

1. General Theory.
2. Theory Applied to Experimental Conditions.
3. Theory Applied to Dilute Ferric Chloride Solutions.
4. Use of Apparatus and Errors Involved.
5. Observations and Their Discussion.
6. Conclusions.

1. General Theory.

Suppose light of intensity i pass through a body of thickness x. Then the rate of change intensity is expressed by the simple formula $di = -kidx$, where i is the intensity at any point and k a constant of absorption depending only upon the wave-length. This gives us, for the intensity of the transmitted light the equation

$$i = i_0 \varepsilon^{-\kappa x}$$

where i_0 is the intensity of the incident light. If the absorbing body be a solution of strength c and length l, we may express x as a function of c and l, or the equation may be written

$$i = i_0 \varepsilon^{-\kappa cl}.$$

If the absorbing system has another component, its equations would likewise be

$$i_1 = i_0 \varepsilon^{-\kappa_1 c_1 l_1}.$$

Since the total transmission is the product of the separate transmissions, we have generally

$$(1) \qquad i = i_0 \varepsilon^{-\Sigma \kappa_\lambda cl}.$$

This equation involves Beer's law,[1] which says that decreasing the concentration will have the same effect upon the transmitted light as decreasing the thickness, or when the product of concentration and thickness is maintained constant the absorption spectra will also be constant. The formula also says that for a system of *n* components represented by $\sum AB$ the absoıption will vary according to the exponential law so long as the components charge uniformily with the concentration. Probably very few experimenters, before the announcement of the dissociation theory, attributed deviations in the observed absorption to changes in the structure rather that to an untenable law.[1] However observations upon isotropic solids uniformly confirm the law. At present we may assume there is nothing wrong fundamentally with the formula, and that it gives us the means of testing the optical properties of solutions. If in our system $\sum AB$, two components A_1B_1 and A_2B_2 partly change so as to form new components A_1B_2 and A_2B_1 or if by dissociation $\sum AB$ yields in part $\sum A$ and $\sum B$, the solutions will show or will not show an apparent variation from Beer's law, according as a certain assumption which we may make is or is not true. If the absorption of a solution is an additive property of its elements, then the absorption of AB is the same as the absorption of $A + B$ and the absorption of $A_1B_1 + A_2B_2$ the same as $A_1B_2 + A_2B_1$ and there could be no change in the simple statement of Beer's law. This would simply mean that the absorption phenomena can give us no information in regard to changes in solution. For changes take place through elements already present in the solution and are not introduced from without. This view of absorption is stated by Gladstone as follows: "From the general rule that a particular base (say B)[2] or acid (say A) has the same effect on the rays of light with whatever it may be combined is aqueous solution, it may be inferred that when two bodies *combine*, each of which has a different effect on the rays of light, a solution of the salt itself will transmit only those rays not absorbed by either, or in other words transmitted by both. Thus if a red acid (A) and blue base (B) combine (AB), the resulting salt will certainly not be purple, but it may present some color intermediate between red and blue." This means that it is impossible to have any apparent deviation from Beer's simple law. If we change Gladstone's statement so as to read do not combine but *coexist* in solution, his statement will then cover very dilute solutions, and his result would be expected. This is a result obtained by Ostwald,[1] who interprets Gladstone's results with this limitation. That there is apparent deviation from Beer's law by chemical reaction is too evident to the unaided eye to need detailed observation. In fact, upon these changes depends the much-employed method of titration. Now it may be questioned whether we have even a right to expect, *a priori* that AB would absorb the same as $A + B$. From dynamical considerations, we may regard the spectral region of absorption of A and B to correspond to the periods of their respective free vibrations. To absorb the same amount in the same spectral region in combination, implies that the product $A\ B$ is executing the vibrations of its original components, or in other words there is no bond of union between them. In general AB must have the characteristic vibration of an independent product, and characteristic absorption. This is not to say that the components do not determine the absorption of the molecule. For a combination in a particular way must affect the vibration in a particular way.

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[1] Pogg. Ann., 86, p. 78.

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[1] A comprehensive review of the literature upon this point is given by Ewan, Phil. Mag. (4), 33, p. 317, 1892. Also in the British Association Reports for 1882 by Dr. Schuster.

[2] Parentheses and italics are the writers.

If a transparent radicle, one whose period of vibration lies outside of the visible spectrum, *combines* with a colored one, dynamically considered, such a system must execute a new vibration. Generally this will displace the absorption bands. The magnitude of the displacement would depend upon the relative importance of the radicles, and this importance at the outset can not be predicted. Observations show that the substitution of a heavier transparent radicle for a lighter transparent one in a colored molecule there is a displacement of the absorption toward the red.[2] The same thing should happen in case of further addition of heavier radicles to the molecule or in the combination of molecules giving more complex molecules. Apparently the combination could displace the absorption so that it did not fall within the limits of the visible spectrum. In case of the coexistence of the components separately, *e. g.*, as ions, the observed absorption would arise from these components only, but the absorption in combination must not be confused with the absorption of such components. The displacement could begin suddenly when any sudden change in the grouping occurs. From dynamical considerations, therefore, color changes in solutions give us a means of testing the structure of solutions, and might in some cases reveal complex molecular aggregates[1] not suggested by other methods.

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[1] Ostwald in Zeit. für Phys. Chem., 9, p. 579, examined the position of the bands for some 300 solutions by aid of the eye and by photography. He concludes that the spectra of dilute solutions of different salts with a common colored ion are identical. Referring to Gladstone's investigations, he says Gladstone's experiments seem to confirm this view.

[2] C. Kruss (Kalorimetrie und Quantitative Spectral Analyse, p. 156, 1891—book not available to the present writer) says that variation in the molecule by replacing H or other element by a radical varies the absorption in a definite sense.

Stenger (Wied. Ann., 33, p. 577), says that change in absorption is parallel to change in properties, *e. g.*, the absorption of rosalin is in the green and the substitution of methyl and phenyl for hydrogen displace the absorption toward the yellow and red respectively.

One method of attacking this problem consists in diluting the solution and increasing the length of the column so as to keep the amount of the solute in the path of light constant and then to observe if there is any shifting of the absorption bands.[2]

Such a difference could only arise from a difference between ΣAB and $\Sigma A + \Sigma B$. The more frequent method is to determine x for each concentration in the general formula. We have then, making c equal to unity,

$$x = -\frac{1}{l}\log_e\frac{l}{l_0}.$$

If i is measured as percentage of i_0, then

$$x = -\frac{1}{l}\log_e i$$

or if common logarithms are used x is the reciprocal of that length which will reduce the intensity of the transmitted light to one-tenth of its original value. The value of x so found throughout the spectrum divided by the concentration of the solution is a constant,

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[1] B. Walter (Wied. Ann., 36, p. 523) says the width of the penumbra round an absorption band is closely connected with the presence of more complex molecular aggregates in solution.

[2] Lippisch (Sill. Journ. (3), 13, p. 304); Russel (Proc. Roy. Soc., 32, p. 258, 1881) found no parallelism between c and l, by this method; and Knoblauch (Wied. Ann., 43, p. 748) observed deviations.

$$\frac{x_1}{c_1} = \frac{x_2}{c_2} = \cdots = \frac{x_n}{c_n}.$$

This constant x has been designated the extinction coefficient,[1] and on account of the convenience in calculating it, it has been extensively used by observers. In both these methods, the *general condition* would indicate a system of absorption curves intersecting each other. For it is clear that each component must have its own extinction coefficient, and on account of selective and overlapping absorption these coefficients not only change from wave-length to wave-length, but also some increase while others decrease. It is also possible, for example, in case of transparent ions to have two systems of absorption curves failing to touch each other at any point. It is further clear that the possibility of observing such a system of absorption spectra depends upon two things, viz: firstly upon a sufficiently sensitive optical system of measurement and secondly upon an appreciable magnitude for the extinction coefficients and an appreciable difference in those magnitudes. It may happen that an extinction coefficient is zero, *i. e.*, its corresponding component is transparent. It may happen that the coefficients are nearly equal. In the system AB yielding in part $A + B$, which occurs upon diluting water solutions, Gladstone's theory requires that the coefficient of the first should exactly equal the sum of the coefficients of the latter two components. The variation in the extinction coefficients is frequently not large, and sometimes within the limits of error of the observations. More generally the fault lies in the ability to command a sufficiently sensitive optical system.[2]

When solutions are studied spectrophotometrically it is not possible to test the optical laws completely and comprehensively in a few months. In the present paper the writer has had time to study but one solution. However, the solution was chosen with reference to its wide range of optical variation. The study of the optical behavior of solutions of ferric chloride was suggested to me by an article by Goodwin upon "The Hydrolysis of Ferric Chloride," studied electrolytically.[1] It was thought that the well-known color phenomena might be followed spectrophotometrically, that there might be a possibility of getting further information either to confirm or refute the hydrolytic theory; that the rate of formation of the final product could possibly be measured; and that some evidence relating to the above dynamical considerations could be obtained. That the presence of hydrolysis and dissociation would complicate the condition was apparent.[2] However, it was thought the phenomena could possibly be separated.[3] How well I have succeeded in this must be judged by the results.

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[1] Bunsen & Roscoe, Pogg., Ann., 101, p. 242.

[2] The Vierordt double slit is the most sensitive arrangement previously used. It does not make use of the Lummer Brodhum principle of the vanishing line. It is further necessary to calibrate the slit, an error generally overlcoked.

2. THEORY APPLIED TO EXPERIMENTAL CONDITIONS.

To study absorption experimentally it is desirable to isolate the components and study each separately. This we certainly can do in the case of isotropic solids, *e. g.*, glass plates. In dealing with solutions, the components in a few cases, *e. g.*, very dilute solutions, can be isolated. Just here, however, the great dilution makes quantitative measurements difficult. Seldom can the components be reduced to one and the phenomenon is necessarily complicated. Solutions must be placed in containing vessels, isotropic solids, which have absorption. Then if the absorption of the solute is desired, we have never less than three components—cell, solvent and solute—over which the summation sign in the general equation extends. Fortunately the cell and solvent may be eliminated. To do this there are several methods of procedure. We may, firstly, take measurements through the empty cell, and then through the cell filled with solution. Corrections according to the Fresnel theory for difference in refraction of glass, air and solution are necessary. Then the ratio of the light transmitted by solution and cell to the light transmitted by the cell alone, gives the light transmitted by the solution.[1] If the absorption of the solute is desired, this value must be divided by the absorption of the solvent. We may, secondly, pass light through a cell of thickness l_1, and then through another another cell of thickness l_2, containing end glasses of identical material. Then the ratio of the readings through the latter solution to those through the former solution give the absorption for a solution of thickness $l_2 - l_1$.[2] If the absorption of the solute is desired, we may proceed as before. This method requires no Fresnel correction. We may, thirdly, use two identical cells, fill one with water and another with solution. Then the ratio of the readings through the solution to the readings through the water give at once the absorption of the solute, when the solution is dilute. When the solution is not dilute two corrections are necessary. One correction due to the difference in the index of refraction of water and solution and another correction due to the fact that the solute displaces an appreciable part of the solvent, whose equivalent thickness is thereby reduced. In the study of the dilute solutions, the third method has been employed. In the study of the more concentrated but thin solutions, the third and second methods were used.

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[1] Zeit. Phys. Chem., 21, p. 1, 1896. Another article continuing this investigation has appeared in the PHYSICAL REVIEW, 11, p. 193, since the present experiments were completed.

[2] Knoblauch, l. c., says, "To test the Arrhenius law, solutions which hydrolize are to be excluded, since the color changes are produced not only by progressive dissociation, but by *chemical variation of the solution*." The italics are the authors and seem practically self evident. Knoblauch would probably accept the further qualification, hydrolizing solutions must be excluded from the test of the Arrhenius law unless measurements are made before hydrolysis begins.

[3] Antony and Giglio (Gazette Chemica, 25, 1, 1895) studied, colorimetrically, the intensity of the blue color, at the beginning and at the end of the colloid reaction, produced by addition of potassium ferrocyanide (quoted from Goodwin as all efforts to obtain this paper were fruitless).

3. THEORY APPLIED TO DILUTE FERRIC CHLORIDE SOLUTIONS.

When we come to apply the theory to the study of dilute solutions of ferric chloride, Goodwin's electrolytic investigations of this solution throw some light upon what may be expected. We have, according to Goodwin, at the outset α ions of $Fe^{\cdot\cdot\cdot}$ and 3 Cl', and β ions of $FeOH^{\cdot\cdot}$, $H^{\cdot}$ and 3 Cl'. At some instant, t, after dilution δ ions of $FeOH^{\cdot\cdot}$ have disappeared, forming with water colloid hydrate $(FeO_3H_3)_x$. We then have at any instant four components $FeCl_3$, $Fe^{\cdot\cdot\cdot}$, $FeOH^{\cdot\cdot}$, and $(FeO_3H_3)_x$ from which we might anticipate absorption. To the unaided eye the very dilute solution appears transparent. This would be prima facie evidence for regarding the components Fe$^{\cdots}$ and FeOH$^{\cdot\cdot}$ transparent. The apparent transparency of the dilute solutions also indicate there is too little of the original product $FeCl_3$ to give an appreciable absorption. (The experimental evidence indicates these components are not as near transparent as is desirable for convenient calculation.) Any color later would then arise from the $(FeO_3H_3)_x$ component and the amount of absorption would be proportional to its rate of formation. Formula (1) than becomes

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[1] Ewan, l. c., p. 327, illustrates the inconvenience of such processes.

[2] Hesse, Wied. Ann., II, p. 876.

$$i = i_0 \varepsilon^{-\kappa_\lambda cl}$$

where the concentration, c, is the only variable. If we take i_0 as unity and measure i in per cent., we have

$$c = -a \log_e i \tag{2}$$

where a is a constant and equals $\frac{1}{\kappa_\lambda l}$, and the cologarithms of the observed transmission are proportional to the product formed. If a solution of known concentration, n_1, is supposed to be A per cent., transformed we have $An_1 = -a \log_e i$, where a is the only unknown. If c is B per cent. of a solution of concentration n_2, we have

$$B = \frac{n_1 A}{n_2} \log \frac{i_2}{i_1}. \tag{3}$$

By sufficiently diluting the solution A can be made to approach 100 per cent. and hence B can be calculated with a fair degree of reliability, provided the solutions n_1 and n_2 are similar in composition and their ratio is not so large as to change the relation of the components. By the electrolytic method B can not be directly measured since the product is not an ion, however, it is formed at the expense of ions, and can therefore be approximated sufficiently well to indicate the general process. To repeat a little from Goodwin's article, if we designate the relative mobility of the Fe$^{\cdots}$, H$^{\cdot}$, FeOH$^{\cdot\cdot}$, and Cl$'$ ions by u, u', u'', and v respectively, we have

$$\mu_{t=0} = \alpha(u + v) + \frac{\beta}{3}(2u'' + u' + 3v) \tag{4}$$

where $\mu_{t=0}$ is the molecular conductivity for infinite dilute solutions.

This formula of Goodwin we may extend to the colloid reaction when we have any instant t,

$$(5)\qquad \mu_t = \alpha(u + v) + \frac{(\beta - \delta)2u'' + (\beta + 2\delta)u' + 3\beta v}{3}.$$

If α decreased no farther during the formation of a colloid, (5) could be written in the form

$$(5a)\qquad \mu_t = \mu_{t=0} + \tfrac{2}{3}(u' - u'')\delta.$$

Then if β ions are entirely transformed into the colloid we have finally

$$(6)\qquad \mu_{t=\infty} = \alpha(u + v) + \delta(u' + v)$$

unless the transformation involves further hydrolysis of the α ions and ultimate change of the entire product into FeOH and free ions of HCl. In which case we have

$$(7)\qquad \mu_{t=\infty} = u' + v.$$

The product, δ, in equations (5), (5a) and (6) corresponds to the product, B, in equation (3). Unfortunately the steps required to obtain δ, and the assumptions made, do not leave the value as accurate as desirable. In the first place, some of the mobility constants must be assumed; secondly the solutions are not infinitely dilute; thirdly we do not know that α remains constant as given in formula (5a) and (6); and fourthly the method which I have adopted to obtain μ from the equivalent conductivities is not free from error. We have a certain equivalent conductivity, x, before the colloid formation. This value will have a certain ratio to $\mu_{t=0}$ which we may express by the equation

$$\mu_{t=0} = mx$$

where m is a constant. We may further assume that this constant relation maintains during the colloid formation. If we then multiply the observed equivalent conductivities in Goodwin's tables by the value of this constant, m, we have values for μ_t during the process of the colloid formation. From these values of μ_t substituted in (5a) we may calculate δ for different intervals during the change.

4. Use of the Apparatus and Errors Involved.

The spectrophotometric measurements were made with the Brace spectrophotometer.[1] The arrangement finally adopted was slightly different from the methods previously described. The light all comes from a single source. The light from one side of a broad thin acetylene flame falls upon one slit. The other side of the same flame falls upon the other slit, so that any fluctuation of the light would cause an equal fluctuation of the intensity before each slit.

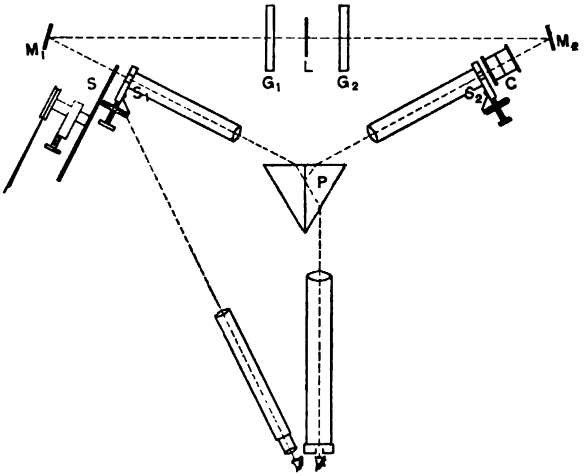

Fig. 1.

In Fig. 1, L is the light, G_1 and G_2 are ground-glass plates, M_1 and M_2 are reflecting mirrors, C is an absorption cell, S is a rotating sector, s_1 and s_2 are slits at the ends of the collimator tubes, P is the Brace prism, and T the observing telescope. Mr. Capps in using this instrument had placed the lights where the mirrors M_1 and M_2 are now located.[2] It is at once seen that any fluctuation in the intensity of one light would produce an error in the readings. Several sources of illumination were tried and none found to be as satisfactory as the incandescent light. However, the light from this source could not be made to cover the solid angle of the slit without the use of the ground-glass plates. This reduced the intensity of his field so much that it became difficult to take readings in the ends of the spectrum. Mr. Capps set about to make incandescent lights which would give large enough solid and uniform illumination to fill the solid angle of the field. After long and patient labor his mechanical ingenuity was rewarded with a satisfactory light. The present writer had neither time nor inclination to learn to make these lights. However, efforts were made to get different lamp factories to make them. Some companies would not furnish them in a small order and other companies forwarded lamps which did not fill the requirements. After wasting some months with these lights, acetylene was finally tried in the positions where the mirrors M_1 and M_2 are placed in the present figure. Obviously any lights burning in an open atmosphere will be subjected to some fluctuations, protected as much as possible. A trial showed that these lights would give all that was desirable in intensity. In fact the field was so bright that one could work with a slit as small as one tenth millimeter. These flames would also fill the field with exceptionally uniform light. Still there was a constant "pumping" amounting to at least one half per cent. The lights were then tried in the position used throughout the experiment. The light was placed in a position L without any ground glasses G_1 and G_2. To cover the entire field the broad side of three acetylene flames were turned together. The mirrors M_1 and M_2 were then adjusted so that corresponding parts of the flame appeared along the vanishing line of the field. Any fluctuating of the flame will now cause a variation in both parts of the field of view and will not interfere with the observations within narrow limits. The light then covers the entire field but not uniformly. To secure uniformity it was necessary to introduce the ground glasses G_1 and G_2. Unfortunately these glasses cut out 98 per cent. of the light which made readings difficult in the ends of the spectrum. Between 4750 λ and 6500 λ results could be obtained which are reliable to within one half per cent., at least so far as the optical measurements were concerned. Farther out in the violet the accuracy diminished rapidly. At 4250 λ the vanishing line disappeared and it became necessary to match intensities as in many other photometers. By removing the ground-glass plates, this difficulty could be somewhat overcome as far as 4000 λ. This, however, left the present light unsatisfactorily distributed in the field. Frequently sets of ten readings have been taken which showed a probable error no greater than one tenth per cent. Then with the plates G_1 and G_2 slightly shifted so as to change nothing but the variable slit readings another set of readings sometimes as accurate as the previous one could be obtained, but the mean result would often differ from the previous result by as much as three fourths of one per cent. This fact seems to indicate that outside the optical measurements personal errors arise. Possibly even in working with the vanishing line, personal judgments in regard to matching intensity are not entirely overcome.

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[1] Phil. Mag. (5), 48, p. 420. Astrophysical Journal, 11, p. 1.

[2] Astrophysical Journal, 11, p. 29.

The solution to be studied was placed in a cell, c, before the slit s_2. The slit s_1 was then adjusted until the line between the fields vanished, *i. e.*, until the fields matched. A sector, S, was also used as well as this slit s_1. By cutting out part of the light with the sector and making the final adjustment with the slit s_1, we can avoid the calibration of the slit, provided we use the sector in such a way as to keep the slit s_1 as near as possible to its original width. It is of course possible to avoid the use of the slit s_1 if we have an adjustable sector of the Lummer Brodhum type. In the present experiments I made use of an inexpensive sector cut into eight sections, used by Mr. Capps in his calibration of the slit.[1] By the use of the sector alone the difference between the two fields could be reduced to one sixteenth, and only this value need be compensated with the slit. Then with a one half millimeter slit, the error in observations arising from the slit can be reduced to one twentieth per cent. This value is certainly negligible in comparison to the errors of the results.

Two cells of the same thickness and having faces of the same kind of glass were used. One cell was used for water, the other for the solution. The water cell was first placed before the slit and readings taken. Then readings were taken through the solution cell and then again through the water to avoid any possibility of fluctuation due to a change in the intensity of the light. Except when studying velocity changes five readings were taken through the water, then ten through solutions and finally five through water. The ratio of the mean readings gives at once the per cent. of the original light transmitted by the solute. The only source of error in this method arose from the fact that the solution persisted in tarnishing the faces of the solution cell and only with the most scrupulous care in cleaning the cell could the absorption be made equal when the two were filled with water.

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[1] Loc. cit.

In the study of the time rate of change of solutions the position in the spectrum was not varied for several days. So that by keeping the ground glasses in the same position, and by keeping the burners clean, practically constant readings through water could be obtained. Readings through water could be taken just before the solution was prepared and then again later as a check when the rate of change in the solution would permit. Sometimes appreciable changes in the water readings occurred when it became necessary to stop the readings of the solution and prepare a new solution. In some solutions the changes were so rapid that only one reading could be taken, but a great number could be taken at short intervals. On account of these changes these solutions were studied for at least three samples for each concentration. Below .0012 normal these solutions show a variation for a given time during the first few minutes changes, as large as two per cent. The first few sets showed values much larger. It was thought that the light had an actinic action upon the solutions and that the difference arose from the length of time the light fell upon the cell. A simple test disproved this. It was known that a small change in temperature influenced the rate of change and a test showed that the trouble in part arose from this source. The solutions were prepared at 25° C. and maintained at that temperature in a constant temperature bath. This bath contained over one hundred and twenty liters of water, was double-walled, and wrapped with asbestos. With a temperature difference between the bath and the room of 5° C. the temperature of the bath would change about one degree in twelve hours, so that it was quite easy to regulate the bath by hand within .05° C. of the required temperature. No attempt was made to regulate the temperature of solutions while before the slit. At the outset some readings were taken and solutions returned to the stock. Although the difference in temperature between the cell and the room during the summer months was very small, it was found that the trouble was at least in part here. Accordingly, the sample used before the slit was thrown away after a few minutes' use, and a fresh sample taken from the stock. This gave more uniform results, but not as uniform as the optical measurements would indicate one might expect. Just what the acting force or source of error may be is to me quite uncertain. Many of the solutions prepared identically, with absorption changes of the same relative magnitude, maintained at the same temperature during the experiment, and subjected only to the fluctuations of the bath after the experiment, were found to be quite different after six weeks. In some cases the more recently prepared solution of a given concentration had entirely precipitated the product and became as transparent as water, while the older solution showed its original color. Some of the stronger solutions (.0016 *n* and .0024 *n*) sometimes showed plainly a marked turbidity before the change had completely ended and at other times they did not. Though the latter solution would not reach the limit of transformation and sometimes began to precipitate at 25° C., a fresh solution heated, could be forced to change completely without any sign of turbidity. These facts lead me to believe that the solutions are very unstable, and that the errors do not arise from optical measurements and temperature changes alone.

5. Observations and Their Discussion.

The ferric chloride was prepared by sublimation. The solution was kindly tested by Mr. R. S. Hiltner and found to have .28 per cent. excess of iron. The concentration, mean of iron and chlorine, with respect to $FeCl_3$ was 3.0779 normal. While a solution prepared from resublimed ferric chloride which was purchased from a reliable firm, Mr. M. E. Hiltner found to have 1.7 per cent. excess of iron. All solutions studied were made from a sample of the former solution of one-tenth the concentration, namely, .30779 *n*. The concentrations of the solutions studied were .0003078 *n*, .0006156 *n*, .000821 *n*, .001026 *n*, .0012312 *n*, .0016416 *n* and .002462 *n* with reference to $FeCl_3$. However, in the tables, these concentrations are designated, for convenience, by their significant figures. The absorption cell in which these solutions were placed was four centimeters long. A layer of the triple normal solution .0032 cm. in thickness contains the same amount of iron as the strongest of the above solutions. We could then for convenience designate both of these solutions by .0024 *n*. Their spectra would be identical if there is no change in the components of the system upon dilution. The thinner layer of the concentrated solution was placed between two plates of clear glass in the form of a wedge. This wedge could be driven at right angles to the slit to the position of desired thickness by means of a micrometer. This method of measuring thickness is certainly not as accurate as an optical method, but is certainly within the limits of the present measurements. These measurements were made upon the thin layer by the second and third methods described in the theory. The readings by the third method were used because the method obviated errors due to changes in intensity of the light. In the study of the diluted .0024 *n* it was however necessary to reprepare five solutions on account of time changes before a complete determination of its absorption spectra could be made, similar readings were made for .0008 *n* in the form of a film and .0008 *n* in dilution. For the latter the values are no more than a rough approximation of the transmission of a fresh prepared solution. The solution cannot be prepared, shaken, and a rough reading taken inside of one minute. During the next minute, in the violet one can see changes that amount to as great as 20 per cent. It was only possible therefore to make a setting, then to set the slit for a little larger transmission and to prepare a fresh solution. After about five trials one could find a setting which did not seem too small when a reading was taken as quickly as possible after the solution was prepared. Similar preparations were required for other points in the spectrum. The values obtained are not therefore the actual transparencies of this solution fresh prepared, but values which the transparencies possibly exceed by several per cent. in the blue. The transparencies certainly do not fall below these values and are therefore significant.

Table I. gives the values by this process for .0024 *n* and .0008 *n* in thin films and in fresh diluted solutions. Columns *a* and *a′* give

TABLE I.

λ	$n = .0024$		$n = .0008$	
	a	*b*	*a*	*b*
5750	99.3	100	100	100
5500	97.9	99.1	100	100
5250	95.8	97.9	99.1	100
5000	92.9	94.8	97.2	100
4750	87.4	90.9	95.7	98.9
4500	70	80.5	84.	94.3
4375	10.9	70.5	51.	90
4250		57.5		83.5
4125				
4000		23		61

transmissions for the films and dilute solutions respectively. It is of interest to compare these values with the transmissions of the same solutions after the colloid formation in Table II. The results are shown graphically in Fig. 5 where the same numbers correspond to the same amounts of ferric chloride before the slit and the letters *a*, *b*, *c*, correspond to concentrated, dilute, and colloid condition respectively. It is evident that diluting the solution makes it relatively more transparent. At 5000 λ the .0024 n in the concentrated form gives a transmission of 93 per cent. In the fresh diluted condition the transmission is 94.6 per cent. From Table X. of Goodwin's results we can infer the degree of ionization of this solution, and therefore also the amount of the original product present. If the ions were transparent this solution should show a transmission of 99.7 per cent. or an absorption of .3 per cent., whereas the absorption observed is 5.4 per cent. This leads to the inevitable conclusion that the ions are not transparent but that their absorption constant is smaller than the constant for the original product. The same conclusion is also drawn from the other concentration and from the other points in the spectrum. Goodwin's results indicate the presence of two positive ions for this dilution and it is apparent that we can not separate the absorption of these ions. However there are seven times as many of the $FeOH^{\cdot\cdot}$ ions as of the $Fe^{\cdot\cdot\cdot}$ ions, and it would seem reasonable to attribute a large part of the absorption to the larger product. Otherwise the

$Fe^{\cdot\cdot\cdot}$ ions would require a much larger coefficient of absorption than the original component. However, diluting the solution further apparently *decreases* the absorption of these ions more rapidly than the dilution. During such a process according to Goodwin, the relative amount of $FeOH^{\cdot\cdot}$ with respect to $Fe^{\cdot\cdot\cdot}$ is *increasing*. This would indicate greater relative absorption for the $Fe^{\cdot\cdot\cdot}$ ion. This action is the only evidence from the present observations to indicate the presence of both $Fe^{\cdot\cdot\cdot}$ and $FeOH^{\cdot\cdot}$ ions, but the observations are not conclusive upon this point.

Table II. contains a spectra study of the solutions after the colloid formation has practically ceased. Fig. 5 shows the results graphically. To obtain the calculated values it is assumed by extrapolation from Goodwin's Table X. that the .0003 *n* is 99.2 per cent. hydrolized at the outset. The assumption of 100 per cent. hydrolysis would not materially affect the calculation. The per cent. transmission of the colloid formation for other solutions is calculated for 5000 λ, since more observations were taken at this wavelength than in other parts of the spectrum. Formula (3) then becomes

TABLE II.

λ	*n*=.002462			*n*=.001231			*n*=.000821			*n*=.000615			*n*=.000308
	obs.	cal.	dif.	obs.	cal.	dif.	obs.	cal.	dif.	obs.	cal.	dif.	obs.
7000	85.5			88.5			93.2			94.4			97.
6500	80.9	81.1	− .2	87.4	88.5	−1.1	91.6	92.3	− .7	93.8	94.1	− .3	97.
6000	73.1	72.7	+ .4	82.9	83.5	− .6	87.6	88.6	−1.0	90.8	91.3	− .5	95.5
5750	56.	56.1	− .1	73.3	72.1	+1.2	79.6	79.9	− .3	85.2	84.8	+ .4	92.
5500	37.	35.3	+1.8	54.8	55.3	− .5	65.9	67.2	−1.3	74.2	74.2	0	86.
5250	16.9	15.3	+1.6	34.2	34.6	− .3	47.8	49.	−1.2	57.8	58.5	−1.0	76.3
5000	5.2	5.2	0	19.2	19.2	0	32.5	32.5	0	42.4	43.2	− .8	65.5
4750				7.7	9.1	−1.4	18.3	20.9	−2.6	30.4	30.2	+ .2	55.2
4500							9.	13.3	−4.3	22.8	22.	+ .8	46.5

$$B = -\frac{\log i}{618 n_2} \tag{3a}$$

and very similar expressions for other points in the spectrum. This gives for .0024 *n*, 86.7 per cent; for .0016 *n*, 90.6 per cent; for .0012 *n*, 98 per cent; and for .0008 *n*, 98.7 per cent; for .0006 *n* the value is assumed to be 99 per cent., which lies between the value for .0003 *n* and .0008 *n*. Now assuming these per cents. and taking the values of i_1 from .0003 *n* column, formula (3) can be used to determine i_2. This gives the calculated values recorded in Table II. In Fig. 5 the observed values are plotted in continuous lines and the calculated values in broken lines. These curves seem to agree as well as could possibly be expected except where the absorption is large in the blue and at 7000 λ. There is however a preponderance of negative differences in the difference columns. Table III. interprets the same readings in another way. Formula (3) is again used. *A*, in that formula, is again assumed to be 99.2 per cent. for .0003 *n* and the readings for this solution are assumed correct. From the observed intensities the per cents. of hydrolysis are calculated for the different concentrations. The variations here appear quite large although in the previous set of observations the differences appeared very natural. But these very differences account for this variation in per cent., since the observed differences are a larger per cent. of the low transmissions than they are of the high transmissions. These results also show that I might have obtained greater uniformity by taking some other solution for standard of reference.

Table III.

λ	*n* = .0024.	*n* = .0012.	*n* = .0008.	*n* = .0006.	*n* = .0003.
6500	86.5	110.	107.5	104.5	99.2
6000	84.8	100.4	107.	104.	99.2
5750	86.3	92.4	101.8	95.4	99.2
5500	81.7	98.9	102.7	98.7	99.2
5250	81.4	102.4	106.	105.	99.2
5000	86.7	98.7	98.7	100.5	99.2
4750		107.	106.3	99.4	99.2
4500			114.	92.8	99.2
Mean.	84.57				99.2

Tables IV. and V. and Fig. 2 show the transmissions of the various solutions during the progress of the transformation. This study was made at 5000 λ, and has been repeated at least three times for each solution. The transmissions in Table IV. are taken to represent the transmissions of the colloid formation. For reasons given

TABLE IV.

Time.		$n=.0003$		$n=.0006$		$n=.0008$		$n=.0010$	
hr.	min.	Intens.	$-\log i$	I	$-\log i$	I	$-\log i$	I	$-\log i$
	2	92.0	.0362						
	4	85.5	.0680			95.6	.0195		
	5	82.2	.0851					95.	.0223
	7			87.2	.0595				
	8	80.0	.0969			90.8	.0419	93.	.0315
	12	77.6	.1101	81.2	.0904	87.0	.0605	90.0	.0458
	16	76.0	.1192			84.0	.0757	87.8	.0565
	20			76.7	.1152	80.2	.0958	85.0	.0706
	26	72.8	.1379						
	30					75.5	.1221	79.0	.1024
	40	69.8	.1561	68.8	.1624	71.7	.1445	74.5	.1278
1	00	67.5	.1701	63.6	.1965	65.0	.1871	68.0	.1675
1	20			60.2	.2204	60.4	.2190	62.5	.2041
1	40			57.2	.2426	57.2	.2426	58.0	.2366
2	00			55.0	.2596	54.8	.2612	54.6	.2628
2	40			51.0	.2924	50.2	.2992	49.3	.3072
4	00			48.0	.3188	45.0	.3468	43.7	.3595
6	00					40.5	.3925	38.7	.4123
6	40			46.8	.3298				
8	00					37.8	.4225	35.7	.4473
19 days		65.5	.1838						
16 "	2 hours			42.4	.3726				
18 "						32.5	.4881		
8 "	3 "							25.	.6021

in discussing Table I., the transmissions of the stronger solutions need some correction before they can be taken to represent the formation of a colloid hydrate. Evidently when i_1 and i_2 are the transmissions of components *A* and *B* respectively, and i the transmissions of the two, $i = i_1 i_2$. At the outset we have no colloid or $i = i_1$. Then the observed transparency at the outset divided into the transparency at any other instant would give the transparency of a new product, provided, the original product remains constant. However the colloid forms at the expense of the other product. We may then assume that the absorption of this product decreases at the same rate the other forms. Then by successive approximations, we may obtain the transmission of a colloid alone. We observe, *e. g.*, i_1, at the outset, and later i, and $i_2 = i/i_1$, for the first approximation. Then $(100 - i_1)\, i_2$ is the approximate absorption of the original product remaining. Then $100 - (100 - i_1)\, i_2$ would be the corrected value for i_1, which divided into i gives the second approximation for i_2. Further approximation is scarcely necessary.

As noted in discussion, Table I., the absorption at the outset may arise from both the iron ions rather than from one and a small per cent., never greater than .3 per cent., may arise from the original product. In this change one of these products, the Fe-OH ion is certainly active and if the other components are active it will make but a trifle difference, and scarcely affect the values obtained by the second approximation. In fact so far as the general course of the formation of the final product is concerned, it is not necessary to assume here any intermediate ion whatsoever. In Tables IV. and V. are also tabulated cologarithms of the colloid transmission. From formula (1) it is evident that these values are proportional to the

TABLE V.

A = Observed transmission. B = Transmission calculated for the hydrolized product.

Time.		$n=.0012$.			$n=.0016$.			$n=.0024$.		
hr.	min.	*A.*	*B.*	$-\log i$.	*A.*	*B.*	$-\log i$.	*A.*	*B.*	$-\log i$.
	2	97.	99.5	.0022	95.7	99.9	.0004	94.6	100.	.0000
	4	96.5	99.	.0044	95.3	99.5	.0022	94.5	99.9	.0004
	8	94.8	97.3	.0119	94.8	99.	.0044	94.3	99.7	.0013
	12				94.1	98.3	.0074			
	14	92.2	94.3	.0255						
	20	89.8	91.9	.0367	93.1	97.2	.0123	94.	99.4	.0026
	30	84.8	86.5	.0630	91.2	95.2	.0214			
	40	80.	81.6	.0883	89.7	92.5	.0339	93.	98.3	.0073
1		71.	77.2	.1415	84.8	88.4	.0535	91.8	97.2	.0123
1	20	64.5	65.5	.1838	78.2	81.4	.0894	89.5	94.5	.0246
1	40	59.1	60.0	.2218	70.8	73.4	.1343	86.5	91.4	.0391
2		54.9	55.6	.2549	63.8	66.	.1805	81.9	85.7	.0670
2	40	48.3	48.9	.3107	57.	52.5	.2798	71.8	74.2	.1296
3					46.	47.4	.3242	66.8	69.	.1612
3	20				43.	44.4	.3526	61.	62.8	.2020
3	40				40.5	41.7	.3788	56.2	58.1	.2358
4		40.4	40.8	.3893	39.	40.2	.3958			
6		34.9	35.1	.4546	31.4	32.3	.4908	34.8	35.1	.4547
8		31.	31.2	.5058	26.7	27.5	.5607	26.2	26.3	.5800
10		26.6	26.7	.5735	24.9	25.7	.5901	21.2	21.3	.6716
14 days.		19.1	19.2	.7167						
22 "					12.5	12.7	.8962			
32 "								5.2	5.2	1.2840

total amount of the product formed. Therefore these values have been plotted here directly and are found in Fig. 3. By dividing these values by the thickness of the cell 4 cm., we obtain the extinction coefficient, the latter divided by the concentration gives the absorption ratio. However these values give no additional information upon the rate of formation. Again the final values of cologarithms *i* in the .0003 *n* are taken to represent 99.2 per cent.

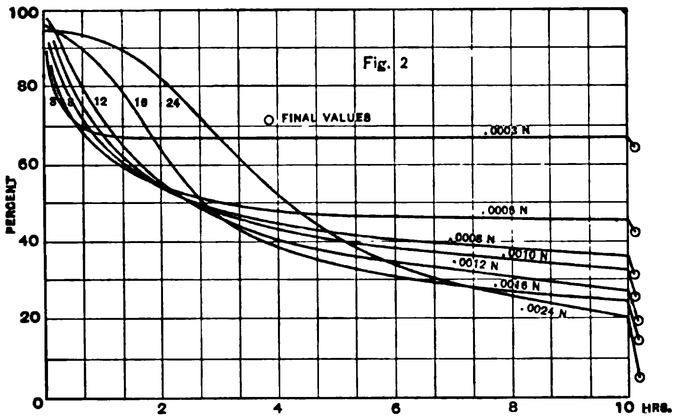

Fig. 2.

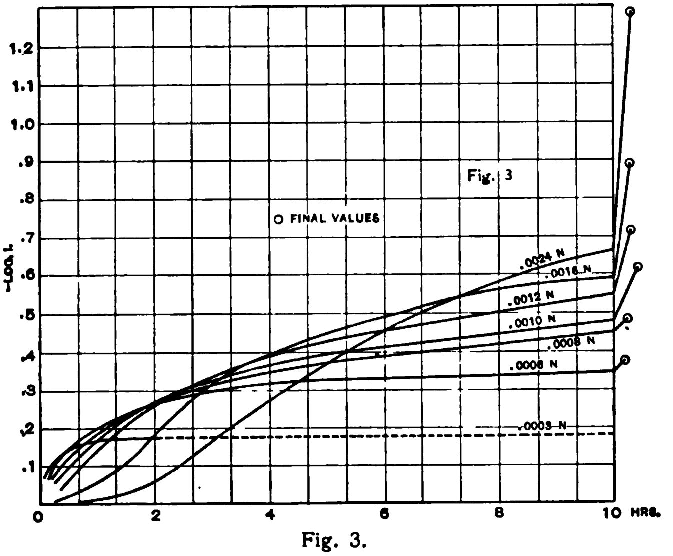

Fig. 3.

transformation and by aid of formula (2) the per cents. transformed for all other values of cologarithms *i*, both for .0003 *n* and other concentrations are calculated. The values of δ are calculated, as indicated in the theory, from Goodwin's data by use of formulæ (5) and (5a). The values so obtained for δ and B are given in Table (VI.) under the names of Goodwin and Moore. The concentrations are according to Goodwin. The values are shown graphically in Fig. 4. This system of curves shows the same general character and indicates approximately the same final condition. The wide gap between the curves at some points I can hardly attribute to the errors in the data of either observer or to the method of calculation. There is a marked tendency, except for the .0024 *n*, for the writer's solutions to begin the reaction sooner than Goodwin's solutions. They behave as if they were warmer. However, I rather anticipate a difference in the solutions, possibly due to a difference in internal condition rather than due to a concentration difference.

TABLE VI.

G = Goodwin. *M* = Moore.

Time.		*n*=.00303		*n*=.000606		*n*=.000802		*n*=.001211		*n*=.0016	*n*=.002422	
hrs.	min.	*G.*	*M.*	*G.*	*M.*	*G.*	*M.*	*G.*	*M.*	*M.*	*G.*	*M.*
	1	3.	10.	0.		0.	3.9					
	4	24.6	36.7	.3					.6	.22		
	10	44.2	56.	2.0	20.8	1.3	10.3		2.2	.6		
	20	59.7	68.4	9.	31.1		19.4	.04	5.	1.24		.18
	35	70.5	80.8			10.1	27.			2.85	.6	
	45			30.5	45.8	21.3		4.2	13.7		1.0	
1	00		91.9	39.	53.		37.8	7.8	19.1	5.4		.83
1	15	84.3										
1	30			52.	61.8	38.4	46.7	18.3	27.4	11.3	2.4	2.37
2	00				70.	46.4	52.8	26.3	34.4	18.3	5.9	4.53
2	30			63.1				32.2	39.4	25.8	9.1	7.63
3	00			66.9	80.8	56.6		37.8		32.6	13.5	10.9
3	30							41 7		37.	17.6	14.8
4	00	94.3			86.	62.8	71.8	45.	52.5	40.	21.5	
5	00			74.		65.		50.2			30.3	
6	00						79.4	55.	61.3	56.6[1]		30.7
•										59.6[2]		
Final		103.6	99.2	104.	100.5	98.	98.7	103.	97.9	90.6	80.4	86.7

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[1] 8 hrs. [2] 10 hrs.

The observed concentration difference of 1.7 per cent. would cause a difference of opposite kind.

It is desirable also to follow these transformations at other points in the spectra. Other wave-lengths will not be so favorable as this one since we can in this position begin with large transmissions, obtain large absorption for small changes and finally large absorption when the product is entirely formed. However, some tests were made at 6000 λ where the absorption seems to form a penumbra. If the absorption at the two points arises from the same molecules, the extinction coefficients should be in a constant ratio to each other. This seems to be true for the final products in Table II.

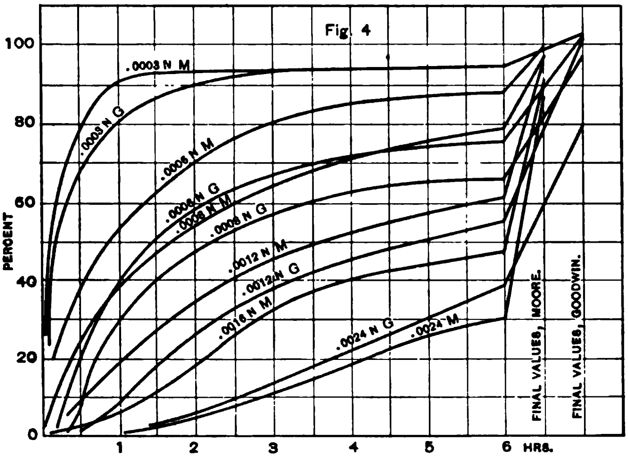

Fig. 4.

The extinction coefficients were so small, however, for the more dilute solutions that the observations, though giving a slight curve could have nearly coincided with previous curves by magnifying them or could have approached a straight line and in either case have been within the limits of error of the observations. It was thought more might be accomplished with the .0024 normal. I tried four solutions of this concentration. The transmissions of these solutions when plotted spread over a field 1.5 per cent. wide. In the early part of the reaction the total absorption after the transformation is practically ended, is only 26.9 per cent. So that a difference of 1.5 per cent. in the early readings makes considerable error in the rate of formation. These readings indicate transformations 10 per cent. larger for .0024 *n* after one and two hours change than at 5000 λ. Plotted as a curve in Fig. 4 they would cross the .0024 *n* curve between 4.5 and 6 hours, but ultimately reach as high a value. If the colloid molecules $(FeO_3H_3)_x$, were not all alike, but if, for some molecules x had one value, and for other molecules another value; and if one set were formed early, in the transformation and another set later, just such action as here observed would take place. Antony and Giglio[1] assumed the presence of $FeCl_2(OH)$ and $FeCl(OH)_2$ in varying proportion depending upon the dilution. Now if we modify this statement and say one product appears early and another later, the selected absorption of the assumed products would produce the observed optical phenomena. Since, however, the final curves show at all points absorption in proportion to the concentrations, it is evident that the ratio of the possible different components is finally the same for all concentrations. The absorption spectra observed could, of course, arise from products of the form $FeCl(OH)_2$. However, from the present standpoint of the theory of solutions and the observations of Goodwin the product $(FeO_3H_3)_x$ may be regarded as practically demonstrated if the final product in solution is FeO_3H_3 we could prepare this solution independent of $FeCl_3$ and test it for identical absorption spectra.[2] The writer may make such an examination later.

In Fig. 5 we find the thin films of a triple normal solution represented .0024 *n* and .0008 *n* to have large absorption bands beginning very suddenly and falling nearly perpendicularly. These absorption bands recede toward the violet when the film is made thinner. From the sharply defined character of the absorption it appears that the molecules have an equally well-defined period of vibration and probably are quite uniform in structure. The presence of well-defined anomalous dispersion in this solution is at once suggested. However, for the colloid formation, the range of molecular vibration is not so uniform. The umbra shades off slowly into a penumbra. Hence again the suggestion of less regularity in the structure of this product. The final curves for the colloid (Fig. 5) are, as previously shown, proportional to the product at all points. This shows that for final examination any mixed red or yellow light could be used in the study instead of spectral lines or the color could be compared with another absorption red.

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[1] Antony & Giglio (reference Zeit. Phys. Chem., 19, p. 191).

[2] Goodwin's recent paper (PHYS. REV., II, p. 193) makes a very similar test, viz.: The accelerating effect of FeOH upon the hydrolizing process.

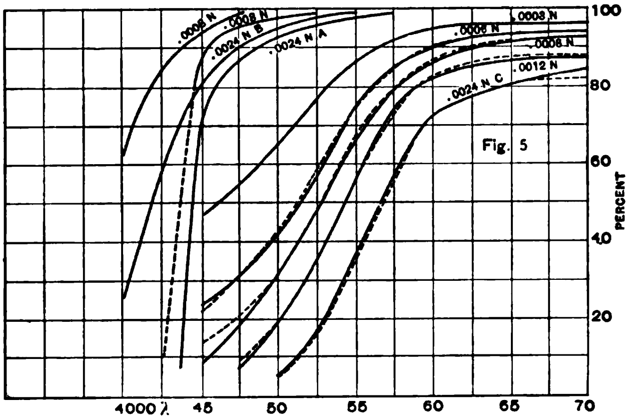

Fig. 5.

6. Conclusions.

1. A study of the absorption spectra has proved to be a good method for following the progressive changes in the colloid formation, and will be serviceable whenever any color changes take place.

2. The presence of ionization is detected and the fact that the ions are not completely transparent is shown.

3. A quantitative determination of the rate of ionization is impossible in the present case, but it is indicated that it is quite possible with some solutions.

4. There is but slight direct evidence for the presence of two iron ions so clearly shown by the electrical method. However, the general agreement of the optical with the electrical methods of finding the rate of formation of the final products gives us further, through indirect, reason for accepting Goodwin's theory of the reaction.

5. There is some, but rather slight, evidence for thinking that the molecules of the final product are not all of the same magni-

tude, *i. e.*, x in the formula $(FeO_3H_3)_x$ may have more than one value for different molecules.

6. The clearing of the solution and the displacement of the absorption bands toward the violet upon dilution ; and the subsequent formation of a much greater absorption band displaced toward the red upon the formation of a more complex molecule, confirm the dynamical considerations.

7. *General Conclusion.*—The optical study of absorption spectra on account of both the optical theory of the relation of absorption to dispersion and the relation of absorption to the molecular structure of solutions should be more general. The method is not as easy to manipulate as the raising of the boiling point, lowering of the freezing point, osmotic pressure or electrical methods ; and by reason of the transparency and general overlapping of the absorption spectra has nowhere near their range of application. However, there is a possibility that the method will show complexity of structure in some cases not brought out by other methods. Further confirmation of results by the other methods is also desirable.

UNIVERSITY OF NEBRASKA, January, 1901.

COHERERS SUITABLE FOR WIRELESS TELEGRAPHY.

By Carl Kinsley.

It is my purpose to show that however much uncertainty attends the use of the wireless telegraph it need not be due to the coherers. It has often been pointed out by the promoters of wireless telegraph companies that the coherers may be relied on in practice. Unfortunately, the scientific experimenter, while presumably impartial, has found coherers unsuited to his purpose, and so by his voluminous writings, has created a popular distrust of an essential part of the wireless telegraph apparatus.

Methods of determining the sensitiveness of coherers have not been used which will enable either the impartial investigators or the practical operators to compare results. I will therefore give in detail the method I have found the most satisfactory in practice in the hope that other experimenters may employ the same or a better one which will enable us to interpret each others results.

For the purposes of wireless telegraphy the most sensitive coherer is the one which, with unchanged conditions at the transmitting station, will receive the signals when its own aërial wire is the shortest. Arrange the apparatus, for the sake of simplicity, so that at the receiving station an insulated aërial wire is attached to one terminal of the coherer while the other terminal is connected to a ground wire. A bypath should be furnished—usually by the local circuit of the recording apparatus—with large self-induction so as to eliminate possible static atmospheric charges. The relative sensitiveness of coherers may be obtained by comparing the length of aërial wire which will always cause the coherer's resistance to fall when the signals are received, with the length necessary for a standard coherer.

The following laboratory method invariably gives the same relative values and it may be called the direct potential difference method of testing. If a coherer has a p. d. between its terminals when its resistance is high—practically infinite—its resistance will be unchanged as the potential is raised until a certain value is reached, when the resistance will suddenly fall. The more sensitive the coherer, the smaller is the p. d. necessary to produce this sudden change in its resistance. This method of rating the sensitiveness of coherers is extremely important, as it may always be used with certainty, and is in no way dependent on the condition of a standard coherer, or of an uncertain transmitting apparatus. Two experimenters[1] seem to have appreciated this characteristic of coherers, but one draws his conclusions from the action of one coherer, and the other merely gives his conclusions without experimental conditions or data.

Many others[2] fail to determine the initial condition of the metals used, and consequently make quantitative results impossible.

The requirements for a satisfactory coherer for wireless telegraphy are few but most important. The coherer must be uniform in its action. Its sensitiveness must be great and must vary but little from time to time. The final resistance of the coherer must fall below some predetermined value after each signal, but it need not be low, as the relay can be adjusted for any value desired.

The performance of particular coherers will illustrate the methods of testing and show how nearly the preceding conditions are complied with in coherers which have been used with entire success for automatic wireless telegraphy. The testing signals were sent at two and one half second intervals. The resistance of the coherer was obtained by calibrating the readings of a very sensitive Weston voltmeter which was connected in series with inductive resistance, the coherer and a source of constant E.M.F. The measuring current was always less than 0.001 ampère.

A coherer may be made so that its final resistance is either dependent or nearly independent of the height of the aërial wire, and consequently of the energy utilized by the receiver. With the transmitter seven miles from the receiver—in New York harbor at stations equipped by the Signal Corps U. S. A.—coherer No. 1, for instance, showed the following values as the results of about 300 observations:

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[1] Trowbridge, Am. Jour. of Sci., September, 1899. Blondel et Dobkevitsch, Compt. Rend., April 23, 1900.

[2] J. C. Bose, Proc. Royal Soc., July 21, 1899. T. Mizuno, Phil. Mag., November, 1900.

COHERER No. 1.

Final resistance = 166 ohms when 150 ft. of aërial wire were used.
" " = 345 " " 100 " " " " " "
" " = 834 " " 75 " " " " " "

Coherer No. 2, however, gave a uniformly low resistance as long as it was affected at all by the electrical waves.

COHERER No. 2.

Final resistance = 18 ohms when 150 ft. of aërial wire were used,
" " = 26 " " 100 " " " " " "
" " = 30 " " 75 " " " " " "

A further slight decrease in the length of the aërial wire caused an entire discontinuation of the signals.

The above coherers were of the same sensitiveness, since each required the same length of aërial wire to effect a change in their normally high resistance. Coherers such as No. 1 can conveniently be used for testing purposes on account of their interesting property of a final resistance depending on the height of the aërial wire. In San Francisco harbor, for instance, where the transmitter was only about two miles from the receiver—between two wireless telegraph signal stations of the Signal Corps of the U. S. A.—the following resistances were observed when Coherer No. 1 was used.

Final resistance = less than 10 ohms when 75 ft. of aërial wire were used with the coherer.

Final resistance = less than 10 ohms when 70 ft. of a. w. were used,
" " = " " 10 " " 55 " " " " "
" " = 33 45 " " " " "
" " = 184 35 " " " " "

The coherer was not affected when 25 feet of aërial wire were used.

If it ever becomes necessary to signal with only 25 feet of aërial wire a coherer more sensitive than the preceding one must be employed. For practical reasons it was not desirable to use a coherer more sensitive than No. 1, and so a wire at least 35 feet long was used. A page of data will give an idea of the variations found in some practical coherers which are entirely satisfactory for wireless telegraphy.

Coherer No. 1.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down:

1.8	2.2	1.7	1.8	2.0	2.4	2.1	2.4
2.2	2.2	2.1	2.6	2.0	2.6	2.6	2.0
2.5	2.5	2.5	1.5	1.7	2.1	1.8	2.1

Average = 2.1

Final resistance after the signal was received:

260	390	570	150	390	230	200	150
200	150	150	110	130	150	390	150
390	150	200	260	150	390	150	150

Average = 234

Again:

260	200	150	260	260	320	110	390
150	200	150	390	200	320	260	200
200	150	200	70	390	260	70	260

Average = 226

Coherer No. 3.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down:

2.4	3.0	3.0	2.2	2.2	2.6	2.8	2.4
3.1	2.6	2.5	2.0	2.5	2.5	2.5	2.0
3.4	2.5	2.5	2.2	1.8	3.0	2.5	2.8

Average = 2.5

Final resistance after the signal was received:

260	150	230	260	320	200	200	260
150	200	150	320	150	230	130	150
200	260	200	390	230	180	230	260

Average = 230

Again:

290	200	200	260	110	260	200
260	260	260	260	200	390	150
150	390	230	530	260	320	260

Average = 259

Coherer No. 4.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down:

5.0	2.6	5.0	4.0	7.0	8.0	5.0	4.0
8.0	5.0	6.0	5.6	6.5	8.0	4.0	4.6
5.2	6.0	5.5	5.6	6.6	6.2	5.0	5.0

Average = 5.5

Final resistance after the signal was received :

70	55	80	70	35	70	130	150
10	15	(*a*)	260	70	10	55	70
150	10	95	55	70	70	70	55

Average = 72

(*a*) The coherer did not break down when the signal came. When tested it was found that 8 v. p. d. were required, showing an insensitive condition. It has thus been found that if a coherer is used which will not break down under 8 v. p. d., it will never be affected by the signals received by that length of aërial wire. Sometimes an increase of two or three feet in fifty is sufficient to put a coherer which was not affected, into operation.

COHERER No. 5.

Sensitiveness as shown by the p. d. in volts at which the coherer broke down :

4.0	4.0	3.8	4.2	3.4	4.0	4.5
3.3	4.2	4.4	4.0	2.6	4.0	3.5
3.0	3.4	4.0	4.0	4.5	4.0	3.8

Average = 3.8

Final resistance after the signal was received ;

700	870	700	570	700	800	1300	320
1005	700	530	870	570	530	570	870
700	700	530	390	1005	870	1300	700

Average = 746

Upon testing the coherers it was always found that as the aërial wire was shortened, the coherers ceased to act always in the order of their sensitiveness. In the case of the above coherers the order was No. 4, No. 5, No. 3 and closely following it No. 1. All of them may be used for receiving wireless telegraph messages automatically, but it will be readily seen that the adjustment of the apparatus when No. 4 is used must be different from the adjustment with No. 5 on account of the difference in their final resistance. If the potential at which the coherer breaks down varies widely, the coherer cannot be used satisfactorily under any circumstances.

The active material of coherers is composed of metal filings. I have refrained from giving the composition of the filings used in the above coherers as I wish to emphasize most strongly the fact that the sensitiveness does not depend on the metal or metals employed. Coherers of any degree of sensitiveness desired may be made of any metal. It is only necessary to treat each metal in accordance with its peculiar nature. In general it may be said that the more readily the metal oxidizes the more carefully must it be manipulated. It is not sufficient to treat every metal in the same way and then from the performance of the coherers to draw up tables of the relative sensitiveness of the metals. It has thus been decided, for instance, that lead filings are too insensitive to be used for coherers. The following coherer illustrates the point. In an atmosphere of CO_2 the lead was filed and placed in the tube which was then sealed, without bringing the filings into contact with the air.

Coherer No. 6.

Sensitiveness as shown by the p. d. in volts at which the coherer breaks down.

0.8	1.0	1.0	1.2	1.1	0.8	1.3	1.4	1.2	1.3
1.1	1.0	1.2	1.2	1.0	0.9	1.2	1.0	1.3	1.3
0.7	1.0	1.2	1.0	1.0	0.9	1.1	1.4	1.1	1.4

Average = 1.1

Nickel is a very satisfactory metal to use, as it can be handled in the open air and can easily be made to give any sensitiveness and ultimate resistance desired for wireless telegraph work. As a final illustration, the test of the sensitiveness of a non-adjustable, exhausted coherer filled with pure nickel filings, and having an ultimate resistance of three hundred ohms is given below.

Coherer No. 7.

Sensitiveness as shown by the p. d. in volts at which the coherer breaks down.

2.4	2.4	2.0	2.2	1.8	1.8	2.1
1.7	2.6	2.4	2.8	2.2	2.4	2.1
1.4	2.0	2.0	2.0	1.8	2.2	2.0

Average = 2.1

This coherer was designed to give a resistance of three hundred ohms after the signals were received, as that was found to be the best value to use with the relays that were employed. This coherer and similar ones have been used with perfect results in practical wireless telegraphy with automatic recorders.

The limit of the sensitiveness of coherers for wireless telegraph work is defined by the p. d. which must always be present between the terminals of the coherer whenever a relay is used. This p. d. should always be kept as low as possible to preserve a safe working margin and thus to prevent any local disturbance from combining with this constant p. d. to produce a temporary p. d. which is high enough to break down the coherer, thereby producing a false signal. It may be of interest to know that the local p. d. I have found best to use is 0.4 volt. As the current must also be kept small—say less than 0.002 ampère—it is obvious that a very sensitive relay must be used. Indeed, it has been found that a relay which will be operated by a current of 0.001 ampère is the most satisfactory.

A GRAPHICAL METHOD FOR ANALYZING DISTORTED ALTERNATING CURRENT WAVES.

BY A. S. LANGSDORF.

THE problem of resolving a distorted wave into its fundamental and harmonics is one which frequently arises in alternating current working, so that a simple solution is of practical interest. The analytical solution, based on Fourier's series, is of course well known, and a number of graphical and mechanical methods more or less dependent upon it have been proposed from time to time.[1] The principal objection to their use is that in some of them several auxiliary irregular curves must be constructed, while in others a planimeter or other integrating device must be at hand. The method described below merely requires the construction of circles and straight lines.

Nearly all of the curves met with in alternating current practice contain only the odd harmonics, so that the wave can be represented by the equation

$$e = a_1 \sin \omega t + a_3 \sin 3\omega t + a_5 \sin 5\omega t + \cdots$$
$$+ b_1 \cos \omega t + b_3 \cos 3\omega t + b_5 \cos 5\omega t + \cdots$$

where $a_1, a_3, \cdots b_1, b_3 \cdots$ are functions of the amplitudes and phase positions of the component sine curves. The complete analysis of the distorted wave requires the determination of these constants. The analytical method is as follows:[2]

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[1] London Elec., Jan. 22–29, 1892, Harmonic Analysis, J. A. Fleming.

London Elec., Feb. 5, 1892, Harmonic Analysis, John Perry.

London Electrician, June 28, 1895, Periodic Functions Developed in Fourier Series, The Graphical Method, John Perry.

Ecl. Electrique, 15, 1898, Harmonic Analysis, S. Berson.

Elec. World, Vol. 31, 1898, Harmonic Analysis, Houston and Kennelly.

Proc. Royal Soc., Vol. XXVII, 1878, p. 371, Sir William Thomson.

Proc. Phys. Soc., Professor Henrici.

Am. Jour. Sc., 5, 1898, Harmonic Analyzer, A. A. Michelson and S. W. Stratton.

[2] Alternating Currents and Alternating Current Machinery, p. 695. D. C. and J. P. Jackson.

Divide the base of one loop of the curve into $(n+1)$ equal parts, so that the angle equivalent to the linear distance between any two

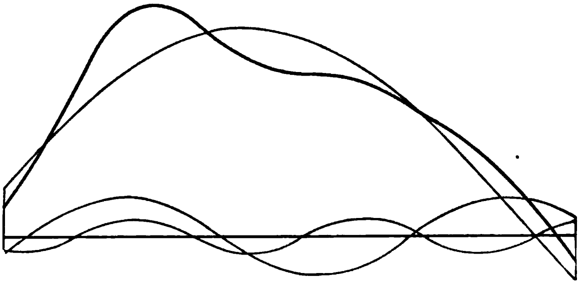

Fig. 1.

points of division will be $\frac{180°}{n+1}$. The ordinate at the (x)-th point of division will then be

$$e_k = a_1 \sin \frac{k180}{n+1} + a_3 \sin 3\frac{k180}{n+1} + \cdots + b_1 \cos \frac{k180}{n+1} + b_3 \cos 3\frac{k180}{n+1} + \cdots.$$

If similar equations are formed for the ordinates at each point of division, there result n equations of the first degree, by means of which the constants, $a_1, a_3, \cdots, b_1, b_3, \cdots$, to n terms can be determined. The general solution for any pair of coefficients, such as a_m and b_m, takes the form

$$\text{(I)} \quad a_m = \frac{2}{n+1}\left[e_1 \sin\left(m\frac{180}{n+1}\right) + e_2 \sin\left(2m\frac{180}{n+1}\right) + \cdots + e_k \sin\left(km\frac{180}{n+1}\right) + \cdots + e_n \sin\left(nm\frac{180}{n+1}\right)\right],$$

$$\text{(II)} \quad b_m = \frac{2}{n+1}\left[e_1 \cos\left(m\frac{180}{n+1}\right) + e_2 \cos\left(2m\frac{180}{n+1}\right) + \cdots + e_k \cos\left(km\frac{180}{n+1}\right) + \cdots + e_n \cos\left(nm\frac{180}{n+1}\right)\right].$$

The significance of these equations from the graphical standpoint can be seen by referring to Fig. 2, which represents in polar coordinates the curve of Fig. 1. Here the original $(n+1)$ equal linear divisions are replaced by the $(n+1)$ equal angular divisions, while the quantities e_1, e_2, etc., are represented by the successive radii vectores.

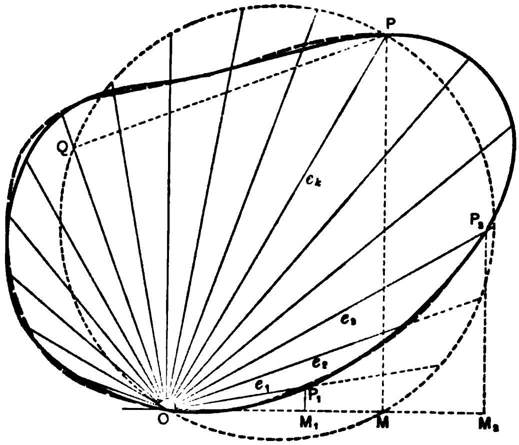

Fig. 2.

Let OP represent the vector e_k; $\angle POX$ will then be $k \cdot \frac{180}{n+1}$; consequently we have

$$PM = e_k \sin\left(k \frac{180}{n+1}\right) \quad \text{and} \quad OM = e_k \cos\left(k \frac{180}{n+1}\right).$$

But these expressions enter into equations I. and II. for the special case in which $m = 1$; therefore if we scale off P_1M_1, $P_2M_2, \cdots$ OM_1, $OM_2, \cdots$ etc., we shall have

$$a_1 = \frac{2}{n+1}(P_1M_1 + P_2M_2 + \cdots) = \frac{2}{n+1} \Sigma PM$$

and

$$b_1 = \frac{2}{n+1}(OM_1 + OM_2 + \cdots) = \frac{2}{n+1} \Sigma OM.$$

Due attention must be paid to the sign of OM.

Inspection of I. and II. shows that the constants corresponding to higher harmonics involve angles which are simple multiples of those used in finding a_1 and b_1. If a circle is constructed on e_k

as a diameter (Fig. 2), the successive radii vectores will intersect its circumference in points such as Q, so that

$$PQ = e_k \sin POQ \quad \text{and} \quad OQ = e_k \cos POQ;$$

if now $\angle POQ$ is made equal to $km \frac{180}{n+1}$, PQ and OQ will correspond to terms in I. and II., respectively; hence,

$$a_m = \frac{2}{n+1} \Sigma PQ \quad \text{and} \quad b_m = \frac{2}{n+1} \Sigma OQ.$$

In order to make $\angle POQ = km \frac{180}{n+1}$, it is only necessary to find a point of intersection on the circumference, which is km divisions from P.

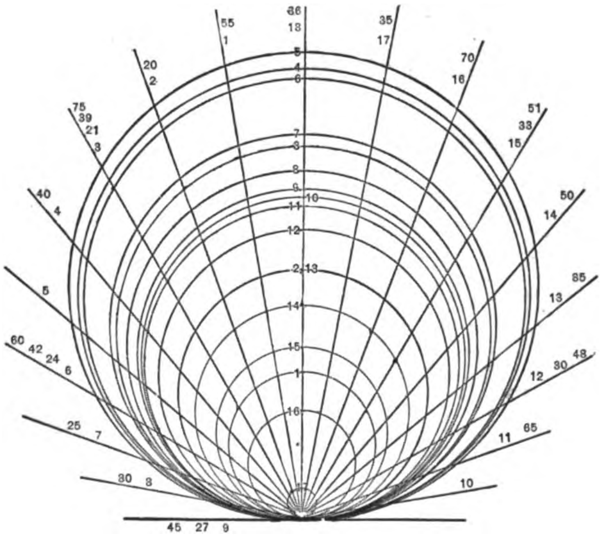

Fig. 3.

In obtaining the summations ΣPQ and ΣOQ it is necessary to pay strict attention to the signs of the constituents. The criteria for the signs of PQ and OQ are as follows:

PQ is *positive* if Q is reached by passing through P an *even* number of times in the counting process; it is *negative* if the number of passages through P is *odd*.

OQ is *positive* if the number of passages through Q is *even;* and it is *negative* if the number is *odd*.

If a circle were to be constructed on each vector in Fig. 2 in order to carry out the above method, the figure would become too complicated for rapid work; this difficulty can be avoided by plotting all the vectorial quantities along a common axis, as in Fig. 3; the circles in this case do not intersect each other.

The following method will be found well adapted for quickly scaling off the required quantities with minimum chance of error.

Number the circles corresponding to e_1, e_2, e_3, etc., 1, 2, 3, etc., respectively; and mark the successive radii vectores ${}_1$, ${}_2$, ${}_3$, etc. (Fig. 3.) Designate the intersection of circle p with vector r by the symbol (p, r); and let $O(p, r)$ represent the distance from this intersection to O, while $p(p, r)$ represents its distance from the vertex of the circle p.

We then have

$$a_1 = \frac{2}{n+1}\left[1(1, {}_1) + 2(2, {}_2) + 3(3, {}_3) + \cdots + N(N, {}_n)\right],$$

$$b_1 = \frac{2}{n+1}\left[O(1, {}_1) + O(2, {}_2) + O(3, {}_3) + \cdots + O(N, {}_n)\right],$$

$$a_3 = \frac{2}{n+1}\left[1(1, {}_3) + 2(2, {}_6) + 3(3, {}_9) + \cdots + N(N, {}_{3n})\right],$$

$$b_3 = \frac{2}{n+1}\left[O(1, {}_3) + O(2, {}_6) + O(3, {}_9) + \cdots + O(N, {}_{3n})\right],$$

$$a_5 = \frac{2}{n+1}\left[1(1, {}_5) + 2(2, {}_{10}) + 3(3, {}_{15}) + \cdots + N(N, {}_{5n})\right],$$

$$b_5 = \frac{2}{n+1}\left[O(1, {}_{15}) + O(2, {}_{10}) + O(3, {}_{15}) + \cdots + N(N, {}_{5n})\right],$$

Usually it is not necessary to go further than this in the analysis of an actual wave. For example, the curves of Figs. 1 and 2 were plotted from the following data:

Angle.	***e***	**Angle.**	***e***	**Angle.**	***e***	**Angle.**	***e***
0	26	50	218	100	152	150	80
10	70	60	206	110	148	160	50
20	118	70	180	120	136	170	14
30	174	80	164	130	118	180	−26
40	210	90	154	140	100		

On analyzing the wave by the method of Fig. 3 (using $n + 1 = 18$), its equation was found to be

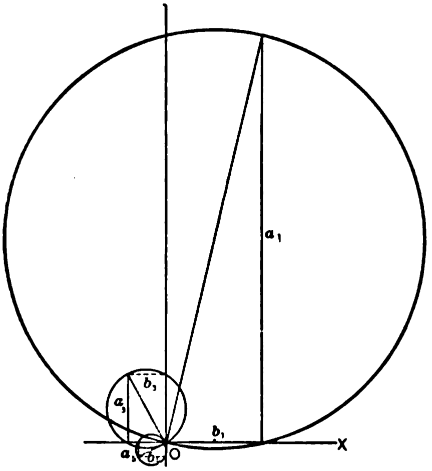

Fig. 4.

$$e = 191.4 \sin \omega t + 31.8 \sin 3\omega t - 6.9 \sin 5\omega t$$
$$+ 44.3 \cos \omega t - 17.5 \cos 3\omega t - 13.3 \cos 5\omega t.$$

In order to check the accuracy of the above equation, the curve which it represents was obtained, and plotted as a dashed line in Fig. 2; it can readily be seen that the two do not deviate appreciably.

In order to form an idea of the relative amplitudes and phase positions of the fundamental and harmonics we may make use of the fact that an equation of the form

$$e = a_1 \sin \omega t + a_3 \sin 3\omega t + a_5 \sin 5\omega t + \cdots$$
$$+ b_1 \cos \omega t + b_3 \cos 3\omega t + b_5 \cos 5\omega t + \cdots$$

may be written

$$\text{(III)} \quad \begin{aligned} e = \sqrt{a_1^2 + b_1^2} \cos \left(\omega t - \tan^{-1}\frac{a_1}{b_1}\right) + \sqrt{a_3^2 + b_3^2} \cos \left(3\omega t\right. \\ \left. - \tan^{-1}\frac{a_3}{b_3}\right) + \sqrt{a_5^2 + b_5^2} \cos \left(5\omega t - \tan^{-1}\frac{a_5}{b_5}\right) + \cdots. \end{aligned}$$

It is thus evident that the amplitude is in each case equal to the hypothenuse of a right triangle constructed on a and b as sides, and that the phase position of this hypothenuse will be correctly shown if *a* and *b* are plotted along the vertical and horizontal, respectively, as in Fig. 4. Circles constructed on these hypothenuses will then represent the component sine waves in polar coördinates.

In recombining these components it must be remembered that corresponding vectors revolve with angular velocities which are to each other as 1 : 3 : 5 ; for example, if the vector of the fundamental occupies the position x°, the third and fifth harmonics will occupy positions $3x^\circ$ and $5x^\circ$, respectively. These angles are measured counter-clockwise from OX (Fig. 4), for which t in equation III. is zero.

In Fig. 1 the light lines represent these component curves in rectangular coördinates.

Ithaca, N. Y., February, 1901.

NEW BOOKS.

Photometrical Measurements. By WILBUR M. STINE. 12mo., 270 pp., 67 illustrations. New York, The Macmillan Co., 1900.

This work, as the subtitle indicates, deals almost exclusively with the photometry of arc and incandescent lights. This would seem to be a matter for regret, as there is no good reason why a manual of "Photometrical Measurements," written with especial regard to the needs of the practician, should not dwell with appropriate fullness upon the peculiar features, which are not a few, of the photometry of oil and gas sources.

The author presents his subject-matter in topical form, which makes the book convenient for reference use. Original sources are frequently referred to—a very commendable feature. In this respect the author has avoided what seems to be a growing tendency among end-of-the-century writers of the technical manual, namely, a tendency towards a fine disregard for sources of information, which manifests, in a work essentially a compilation, more brevity than courtesy. One reads in the preface that the work has been written "from the literature of photometry and with little reference to existing works on the subject." This, of course, is as it should be.

Chapter I. deals with such physical and physiological light phenomena as are likely to enter into ordinary photometric practice. The next chapter, which through a typographical error is also numbered I., treats of the laws of distance and inclination, of *illumination*, *intrinsic brightness* and other fundamental notions. The author argues well for the abandonment of the name *candle-power* and the substitution of the name *light unit* pending the development of a satisfactory light standard. The author considers the *quantity of light* emitted by a source of intensity I as $4\pi I$ units, as does Palaz in his well-known treatise. Blondel, on the other hand, calls this magnitude *luminous flux*, while reserving the term *quantity of light* for the product flux × time. This latter usage has much to commend it, both by way of physical analogy and practical value. The concept of flux × time, or more often, intensity × time, is used constantly by practical men under the guise of *candle-power hours*, and is of evident utility. Whether we are ready or not ready for a new word for each photometric quantity, there can be no question as to the need of having a given term mean one thing and one thing only.

In his discussion of the method of finding the mean spherical intensity from a meridional section of the photometric surface, the author makes a serious blunder. One is told to take the area of the given polar distribution curve and to draw a circle of equal area. The radius of this circle is the value sought! Had the author written the usual expression for the area of a polar curve instead of the double integral of equation (39), he could hardly have failed to note that the area of such a curve is a function of the square of the radius vector and hence the equivalent circle has a radius equal to $\sqrt{\text{mean square.}}$ To borrow from the terminology of alternating currents, this process leads to the *virtual candle-power*. It is doubtful if our most enthusiastic advocates of a revised photometric nomenclature are prepared for this. In the hypothetical distribution curve given as an example, namely two circles tangent at a given point in a vertical line this method leads to .707 × maximum intensity, whereas the true mean spherical intensity $[\frac{1}{2}\int_0^\pi I_\theta \sin\theta d\theta]$ is .785 × the maximum intensity. Again, in Art. 231, the reader is told to obtain the mean spherical intensity of a glow lamp by the same erroneous method. In Appendix A, which deals with the results of Williamson and Klinck on the absorption of various globes over a mantle burner, the author says: “ * * * the mean spherical candle-power was calculated by the methods already explaimed.” The figures accompanying the text show plainly that the integration was performed by the classic method of the Rousseau diagram.

The subjects of Photometers and Light Standards are taken up in an able manner in Chapters III. and IV. These two chapters cover a good half of the book and furnish an excellent *résumé* of the subjects, without too great description of apparatus whose value is chiefly historical. Naturally, the greatest prominence is given to the Bunsen and Lummer-Brodhun screens, and to the amyl acetate standard. No mention is made of the very carefully elaborated Blondel-Broca universal photometer. Article 179 on the working values of light standards will prove very useful to one who wishes to compare the results of different observers. The author neglects to state in this connection that the Geneva Congress (1896) decided that, for practical purposes, the *bougie décimale* would be considered as represented by the Hefner lamp.

In Chapter VI. the photometry of the glow lamp is well discussed. The concluding chapter on arc-light photometry is hardly as complete as one could wish for. The devices designed by Houston and Kennelly and by Blondel for giving directly the mean spherical intensity might well be given some notice here.

As a whole the work will be useful to students of the subject, but the errors to which attention has been called should receive early correction.

C. P. MATTHEWS.

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THE PHYSICAL REVIEW.

EXPERIMENTAL STUDIES ON THE RESONANCE OF CONICAL, TRUNCO-CONICAL AND CYLINDRICAL AIR-COLUMNS.[1]

By Victor Mahillon.

1°. All persons who have studied organography know how many prejudices are still to be encountered and how indispensable is the assistance of acoustics in shedding light on obscure points. It must be admitted that the manufacture of breath instruments, undoubtedly the most complicated of all branches of instrument making, is exactly in proportion to its importance and difficulty, the one in which this unfortunate state of affairs is most marked. False theories founded on insufficiently studied facts abound; empiricism is about the only guide.

The author has not escaped from errors caused by this situation. It costs nothing to confess this, and, furthermore, the beginnings of the catalogue are there to bear witness to this fact. But these errors could not be avoided; therefore they will be forgiven for this good reason, in the first place, and, in the second, because the evident proof of a constant search for the truth will be found alongside of each mistake.

It is not claimed, by any means, that full light has been cast on this branch of organography by thus setting forth and grouping together the results of a long series of patient trials. One thought only has prevailed through it all, that this work may be useful, by setting forth the fruits of much toil, in saving those who come after us from falling into similar errors. It is believed also that these investigations will be useful in still another way. It is this—as they were made on all sorts of shapes of tubes and on all sorts of ways of producing vibrations, they have revealed hitherto unnoted phenomena, a knowledge of which will assist, to a certain though undoubtedly modest extent, in determining the laws which govern the vibrations of air-columns in a way more exact than that now taught by acoustics.

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[1] This paper is a translation by Major F. A. Mahon, U. S. Engineers, of the original account of studies carried on for nearly twenty-five years by M. Victor Mahillon while bringing together and cataloging the collection of the Museum of Instruments of the Conservatory of Music, at Brussels. [See Catalogue de la collection instrumentale du Musée du Conservatoire Royal de Musique à Bruxelles, par M. Victor Mahillon, Conservateur du Musée.]

2°. In order to facilitate the setting forth of the subject, the principal laws, as now laid down, will be called briefly to mind. Observations on these laws will be reserved for the special cases which will arise in the course of this study.

The length of an open tube is equal to that of a single sound wave; the length of a stopped tube of the same pitch is equal to the half-length of the same wave.

The length of the single wave is the space traversed in the surrounding medium, the air, by the vibratory motion imparted to this medium by a single vibration of the vibrating body.

The velocity of 340 meters per second is that generally adopted in calculations for the propagation of the vibratory motion.

3°. The author has stated already, in his *Essay on Classification*,[1] that the opinion which he holds on the subject of sound and its formation differs not a little from that which is accepted generally. He maintains that sound is exclusively the result of the vibratory motion of the surrounding air, and that no air no sound. This importance is not given to the air as a mere vehicle; the author believes that the motion of the air is the very sound. This motion, which is silent until it strikes the auditory apparatus, only becomes really sound at the very moment of impact.

Three principal qualities are recognized in the sensations of hearing: *intensity*, arising from the force with which the vibratory motion in started; *pitch*, or degree of acuteness, which depends on the rapidity of this motion; and finally *timbre* or tone quality, which results from the more or less complex shape of the vibratory motion imparted to the air.

The tone quality of instruments is distinguished solely by the form of the vibratory motion given to the air, and by the relative intensity of the fundamental sound and its harmonies. There is no sound of steel, wood, strings, etc.; there are only different vibratory motions imparted to the surrounding medium, their effects being designated and distinguished by the use of terms which recall their origin.[1]

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[1] Catalogue du Musée, t. I., 2de édition, p. 1.

Temperature in degrees Fahrenheit.	Temperature in degrees Centigrade.	Velocity of sound in meters per second at the indicated temperature.	Number of vibrations given at the indicated temperature by a tube tuned to 870 single vibrations at the temperature of 15° Centigrade.		Length of the wave produced by a sound of 870 single vibrations at the indicated temperature.	
			Single vibrations.	Double vibrations.	Single waves open tubes.	Half single waves stopped tubes.
32.	0	332.	847.03	423.51	0^{m}.382	0^{m}.191
33.8	1	332.6	848.56	424.28	.382	.191
35.6	2	333.2	850.09	425.04	.383	.191
37.4	3	333.8	851.62	425.81	.384	.192
39.2	4	334.4	853.15	426.57	.384	.192
41.	5	335.	854.68	427.34	.385	.192
42.8	6	335.6	856.21	428.10	.386	.193
44.6	7	336.2	857.74	428.87	.386	.193
46.4	8	336.8	859.27	429.63	.387	.193
48.2	9	337.4	860.80	430.40	.388	.194
50.	10	338.	862.33	431.16	.389	.194
51.8	11	338.6	863.86	431.93	.389	.194
53.6	12	339.2	865.39	432.69	.390	.195
55.4	13	339.8	866.93	433.46	.390	.195
57.2	14	340.4	868.46	434.23	.391	.195
59.	**15**	**341.**	**870.**	**435.**	**.392**	**.196**
60.8	16	341.6	871.53	435.76	.393	.196
62.6	17	342.2	873.06	436.53	.394	.197
64.4	18	342.8	974.59	437.29	.394	.197
66.2	19	343.4	876.12	438.06	.395	.197
68.0	20	344.0	877.65	438.82	.395	.197
69.8	21	344.6	879.18	439.59	.396	.198
71.6	22	345.2	880.71	440.35	.397	.198
73.4	23	345.8	882.24	441.12	.397	.198
75.2	24	346.4	883.77	441.88	.398	.199
77.	25	347.	885.30	442.65	.399	.199
78.8	26	347.6	886.83	443.41	.400	.200
80.6	27	348.2	888.36	444.18	.400	.200
82.4	28	348.8	889.90	444.95	.400	.200
84.2	29	349.4	891.43	445.71	.401	.200
86.	30	350.	892.96	446.48	.402	.201

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[1] Let it be borne in mind that if the walls which confine the air-column and give it its shape be sufficiently smooth and stiff, the material of which they are made has no effect on the shape of the vibration and, consequently, it has no influence on the quality of the sound.

The velocity of sound, continuing to use the consecrated term, increases with the rise of the temperature of the air; hence this rise should be considered in calculating the length of waves and tubes.

The table on previous page gives the effect of temperature on a tube tuned to A, the 58th degree of the scale of sounds.[1]

It is seen by this table that the influence of temperature has a value which may not be neglected. The velocity of propagation varies by about 60 centimeters per second,[2] and the rate of vibration of the A of 870 single vibrations per second also varies by 1.5308 single vibrations for each centigrade degree of temperature. It follows from this that an open tube giving this A would be 382 millimeters long at the temperature of melting ice (0° Centigrade, or 32° Fahrenheit), whereas at 30° C. (86° F.) the same A would require a tube 402 millimeters in length. The intonations of these two tubes, compared at the same temperature, would vary by a full semi-tone.[3]

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[1] The *C*, the first degree of the lowest octave, the one known in organ-building as the 32-foot octave, is taken as the starting point. From this is obtained the following scale with all its intermediate degrees:

1st octave,	*C* 1st degree,	6th octave,	*C* 61st degree.
2d "	*C* 13th "	7th "	*C* 73d "
3d "	*C* 25th "	8th "	*C* 85th "
4th "	*C* 37th "	9th "	*C* 97th "
5th "	*C* 49th "	10th "	*C* 109th "

By means of this method, approved and recommended by the international jury of the Universal Exposition at Brussels in 1897 (G. Serpette, Rapport sur les opérations du jury), the position of a sound is determined more than easily by the use of indices which have no base and which vary from one country to another.

[2] John Tyndall, On Sound, p. 26.

[3] This effect of raised pitch is still more marked for wind instruments whose air-column is set in vibration by the breath. The effect of the latter, of which the mean temperature is 32° C., or 89.6° F. (according to Gréhant, cited by Kuss and Duval—Traité de Psysiologie, p. 434—the temperature of the breath is 35.5 at 22° and 29.7 at 6°), is, in our climates, where the surrounding temperature is generally below this figure, to warm the air-columns, to increase the rate of vibration, and, consequently, to cause the pitch to rise very sensibly; the colder the air the more marked is this effect. These facts have an important bearing on the tuning of wind instruments. The mean temperature of concert halls, especially in winter, being about 20° C. (68° F.), *all* instruments without exception should be tuned at this temperature. A unison would be obtained in this way between those which are less sensitive to temperature, piano and harmonium, for example, and those more sensitive to this influence, such as the organ and all wind or breath instruments. Before the latter are regulated they should have been played for some minutes.

4°. Assuming the velocity of the propagation of sound generally adopted for acoustic calculations, viz: 340 meters (1,115 feet) per second, this number must be divided by the number of single vibrations per second if the length of the sound wave be desired, this length being the space traversed by the vibratory motion of the air during a single vibration of the vibrating body. Thus the length of the single wave corresponding to the A, 58th degree of the scale of sounds, is obtained thus:

$$\frac{340 \text{ meters}}{870 \text{ single vibrations}} = 0.39 \text{ meter.}$$

5°. Theoretically, therefore, an open tube 0.390 m. long should give the A of 870 single vibrations, and this same sound should be produced equally well by a stopped tube

$$\frac{0.390}{2} = 0.195 \text{ m. long.}$$

6°. Practice shows that these data are inaccurate, or at least incomplete. If the air be made to vibrate in the two cases, by blowing into these tubes in such a way as to set their air-columns in motion in the simplest way, that is, by blowing across the open orifices of the tubes held firmly against the lower lip, sounds will be obtained sensibly lower than the A of 870 single vibrations, and it has been noticed further that the stopped tube gives a slightly lower sound than the open tube.

7°. To what cause must this difference between the teaching of theory and that of practice be assigned? To this circumstance, it is believed; that the influence of the tube is felt beyond its bound-

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In like manner the air sent into the pipes of an organ by the bellows should be brought first to a temperature of 20° C.

The French commission of 1859, when it fixed the pitch of the A_3 (58th degree of the scale of sounds) at 870 single vibrations with a temperature of 15° C. (59° F.), wished only to state absolutely the conditions under which the vibrations of the standard had been attained. The idea that it wished to set at 15° C. the temperature at which instruments should be regulated according to its *tonarium*, cannot be attributed to it. Furthermore, it would be impossible to maintain this temperature, whereas 20° is the temperature of our halls, as a general rule, at all seasons of the year. It is known that the influence of temperature on steel tuning forks is so small that it can be regarded as nothing in practice. This circumstance should cause them to be preferred to any other apparatus intended to give the pitch.

aries, thus causing a wave longer than the theoretical wave and, consequently, a sound lower than the one expected.

8°. This difference was something interesting to examine closely, and led naturally to studying it in its results on the different shapes of tubes used in the construction of wind or breath instruments. These shapes appear under three main categories: *open tubes; partly stopped tubes; stopped tubes.*

9°. But while belonging to one of these three categories, tubes may differ very sensibly in their details. All the special shapes met in the course of these studies have been summed up by the making of eleven tubes. These tubes, shown in outline in Fig. 1, vary between 0.290 m. (11.42 inches) and 0.240 m. (9.45 inches) in length; the figures at the end show the diameters in millimeters at those points, and the accompanying letters will be used hereafter to designate them.

I. OPEN TUBES.

10°. The tubes thus named are entirely open at both ends. Hence their air-columns are in communication with the surrounding air at each extremity; whence follows the existence at each end of a loop of vibration for all the sounds of its harmonic resonance. The loop of vibration is that part of the wave where the air has a maximum motion of vibration without any change in pressure or density. At the node of vibration, on the contrary, the air undergoes continual changes of density and pressure while the velocity of the vibratory motion at test point is zero. The fundamental sound and the harmonics of open tubes are to each other as the natural series of whole numbers 1, 2, 3, 4, etc. The fundamental sound of a tube is the lowest sound which it can give. It is the one corresponding to the calculated length of the tube. It is produced by the least pressure exerted on the air-column to excite its vibratory motion.

Experience shows that it is very difficult to cause columns of air, set in motion by blowing across one of the orifices of the tube, to produce sounds of a certain intensity. Still the motion of the air-column resulting from this form of winding is sufficient to determine very accurately the height of the sound, and, with a little practice, a certain intensity is imparted to it. With perhaps one exception, the *Nay*, the flute of Musulman countries, this style of tube has not been used in the manufacture of instruments. The *Nay* itself is not a wholly open tube at its upper end, because, in order to facilitate setting the column of air in vibration, the performer partly covers the opening of the tubes with his lips (see § 15).

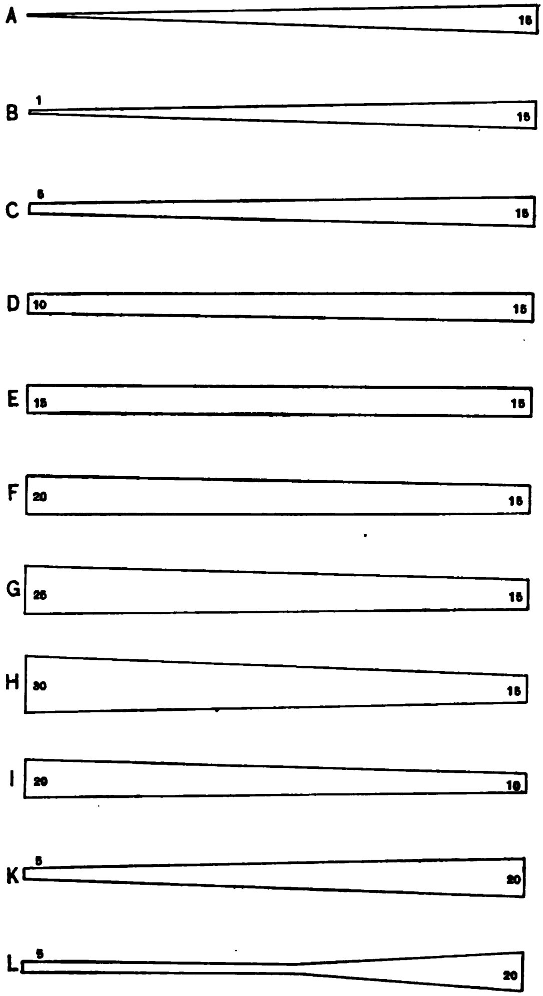

Fig. 1.

11°. It has been stated (§ 6) that, when experimenting with a tube of exactly the length of the sound wave, a deeper sound than that indicated by theory is obtained. Numerous trials show that the difference between the data of theory and those of practice increase with the diameter of the tube. If the sounds of two cylindrical tubes of the same length but of different diameters be compared, the sound of the tube having the smaller diameter will be sensibly higher than that of the other. The observation of this fact gave the direction in which to seek the following formula of correction, noted already in 1874.[1]

The length of a cylindrical tube open at both ends is, for a given sound, equal to the length of the single wave of this sound less a length equal to ¾ of the diameter of the tube. It has been seen (§ 4) that the length of the single wave of a sound of 870 single vibrations per second is 390 mm. If a tube 20 mm. in diameter be required to produce this sound its length will be:

$$390 - 20 \times \tfrac{3}{4} = 375 \text{ mm.}$$

In fact, an open tube of this length set in vibration in this way, gives exactly the normal A of 870 single vibrations at the temperature of 14° C. (57.2° F.).

Another and equally important result follows from this fact, viz: that theory lacks in accuracy when it teaches that, to cause one tube to give a sound an octavo lower than the sound of another tube, the length of the first tube should be double that of the second. *It is the theoretical length of the wave which must be doubled,* and this doubled length must be lessened by ¾ the diameter of the tube. Thus, to obtain an A of 435 single vibrations from a tube 20 mm. in diameter, the theoretical length of the wave corresponding to the A of 870 single vibrations is doubled, and from that is taken three-fourths of the diameter of the tube:

$$390 \times 2 - 20 \times \tfrac{3}{4} = 780 - 20 \times \tfrac{3}{4} = 765 \text{ mm.}$$

A tube of these dimensions will give very accurately the A of 435 single vibrations at the temperature of 14° C.

12°. The following results are obtained from general observations on the eleven before-mentioned tubes:

(*a*) The pitch of the sound produced by blowing across the end of the tube is the same whether the breath be applied at the large or the small end.

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[1] Eléments d'acoustiquemusicale, by V. Mahillon.

(*b*) The length of each of the eleven tubes tried is that of the single wave less three-fourths of the mean diameter.

(*c*) The harmonics obtained are proportioned to the fundamental sound of the tube. This sound is very exactly the F of 1,381 single vibrations (66th degree of the scale of sound corresponding to the normal pitch). The wave of this sound is, as shown in § 4, equal to $\frac{340}{1381} = 246$ mm. as shown in the following table :

Real length of the tube.	Length of ¾ of diameter.	Length of the single wave.
A $0^{m}.2404$	$0^{m}.0056$	$0^{m}.246$
B .240	.006	
C .2385	.0075	
D .2366	.0094	
E .23475	.01125	
F .2329	.0131	
G .231	.015	
H .2291	.0169	
I .23475	.01125	
K .2366	.0094	
L .2366	.0094	

As will be seen further on, an exception is made for the tube *L*, which is irregular in shape, the cylindrical tube being prolonged by one of trunco-conical form.

13°. When each of these tubes is examined by itself from the standpoint of facility in starting the vibrations of the inclosed air-columns it is noticed :

1. blowing across the small end :

(*a*) That *A*, *B*, *C*, *K*, *L* do not speak. *A* is wholly closed at the apex of the cone ; it will be considered further on. The opening at the narrow end of *B*, *C*, *K*, *L* is too small to allow the vibration of the air-column to be excited.

(*b*) That *D*, *E*, *F*, *I* speak easily, and, in addition to the fundamental sound, allow the octave, or sound 2, to be given.

(*c*) That *G*, *H* give the fundamental sound easily, and the octave with greater difficulty.

2. blowing across the large end :

(*a*) That *A*, although wholly closed at the vertex of the cone, acts as an open tube, that is, contrary to theory, its length for a given sound is equal to the single wave of that sound and, in spite of its being wholly closed, it gives the series 1, 2, 3, etc., of the harmonic scale and not the odd-numbered ones alone.

(This peculiarity of conical tubes closed at the vertex was discovered first, it is believed, by the celebrated English physicist Wheatstone about 1832. It has been mentioned already in D. J. Blaikley's very remarkable study, *Acoustics in Relation to Wind Instruments*. This very important fact will be taken up again further on.)

(*b*) That *B*, *C*, *D*, *E*, *F*, *I*, *K* speak well and give easily the harmonics 2 and 3, in addition to the fundamental sound.

(*c*) That the sonorous starting (*ébraulement sonore*) of *G*, *H*, is difficult on account of their great diameter, which interferes with the production of the oscillatory motion necessary for this starting.

As these eleven tubes give the same sound F, 66th degree of the scale of sounds, it may be concluded from the preceding experiments that the effect of the bore on tubes set in vibration in the same way is almost nothing so far as the pitch of the fundamental sound is concerned, or at least that it exerts no greater influence than that mentioned in § 1·1. It may be well to remark that for tubes of the same length harmonics are produced rather more readily by tubes of the smaller diameter.

It has been said (§ 12) that *L* is a tube of irregular shape. If the vibratory motion be given at the large end, the fundamental sound rises a fourth, while the harmonics remain those of the tone F, common to all the other tubes. It has been observed, by experiments on other tubes, that the pitch of the fundamental sound rises as the broken lines which form the sides of the tube approach the axis more nearly, or, in other words, as the tube becomes narrower. This peculiarity of this kind of tube is not of great importance, as tubes wholly open at both ends are rarely used in manufacturing; it does permit to be noted however that the irregular shape of the tube *L*, for the mode of applying the breath under consideration, gives a harmonic resonance which is false when compared with that of the regularly shaped tubes: cylindrical, conical and truncoconical.

II. Partly Stopped Tubes.

14°. The material impossibility of producing in tubes of large sectional area, either by the breath or even by mechanical means, the pulsations necessary to set the air-column in vibration, has caused the manufacturing industry to seek some arrangement which would permit the required action to be produced on thin sheets of air or on reduced sections. Hence, the different shapes of the mouth opening devised from time immemorial among all nations, and still utilized to-day in making all the varieties of flutes used in the organ as well as in our orchestras. Among the latter the most familiar varieties are the *flute à bec*[1] and the *traverse flute*. In both types the tube was partly closed so as to allow a thin sheet of air to be directed against the sharp angle formed on one of the sides of the tube, an arrangement which gave extreme facility in the production of the vibratory motion.

15°. The practical demonstration of this facility of sonorous emission is easy: let the tube *E*, for example, be taken. If it be held vertically against the lower lip, so as to direct the breath over the whole section of the tube, a certain amount of practice will be necessary in order to obtain a sound. But let the tube be raised so as to give it an inclination of about 45° ; then let the breath be directed against the edge opposite to that touched by the lip, care being taken to cover nearly half the orifice of the tube. The latter will speak with very great facility, and will give out a full, pure sound. The construction of the Arabian *nay*, the mode of setting which in motion has been so little understood by some historians, is based on the observance of this principle.[2]

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[1] It seems easy to-day to establish the parentage of the flute à bec. The primitive type appears to have been the Arab *nay*, which was completely open at its ends; then the *siaku-hachi*, a Japanese flute, in which the end of the tube is bevelled on a part of the circumference to facilitate setting the air-column in vibration. The next step seems to have been the Chinese *lu*, of which the orifice is entirely open, but on the circumference of which was cut a small rectangular notch, the breath being directed against its edge; this same notch is found again in the flute Krena, from Bolivia; finally the Chinese *ty*, also with the rectangular notch, but closed at the orifice by the tube, thus forming a true bevelled mouth. (See Nos. 136, 714, 859, 862 and 711 of the *Catalogue du Musée.*)

[2] In describing the *lus*, or Chinese pitch pipes, Nos. 859, 860, 861 of the Catalogue du Musée, mention was made of the theory set forth in 1596 by the Chinese Prince, Tsai-Gu, on the subject of the relation to be maintained between the length and the

16°. The partial closing of the tube, by causing an inevitable slackening in the velocity of vibration, brings about a lowering of the pitch. And all our flutes give lower sounds than those indicated by theory, even when the lowering due to the diameter has been considered. It cannot be otherwise; all flutes are partly closed at the mouth hole, and the smaller the opening used for exciting the vibratory motion the greater the lowering of the pitch. The evidence seems to be that the partial closing demands a tube of a certain diameter, while, on the other hand, narrow tubes must be used to facilitate the production of the harmonics. The oldest makers of the flute *à bec* overcame the difficulty happily by using a trunco-conical bore; they had thus at their disposal the wide part at which to place the mouth, and in order to assure facility of emission, a relatively narrow air-column, or at least one much more narrow than a cylindrical air-column would have given. This is not the case with a *traverse* flute; the side mouth by which the air-column is set in vibration does not require a wide opening, therefore the old *traverse* flutes were cylindrical as they are to-day. It was only in the seventeenth century that instrument makers, imitating the flute *à bec*, adopted the trunco-conical shape of the air-column, placing the mouth hole at the largest part of the tube.

17°. A question arises here, Is it possible to calculate the lowering which this partial closing causes in the pitch of the tube?

It is very difficult. But, what numerous trials have given the means of noting, is this: *the influence of this closing is inversely proportional to the length of the tube*, and this is a fact of a certain weight. Beyond this the result obtained must be determined experimentally.

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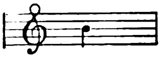
diameter of the pipe. According to this theory, in which the author, by reason of his studies, could not help being interested, the lengths and diameters increased in a constant ratio. The analysis of this theory showed that the length increased for each of the twelve descending semi-tones of the octave in the ratio of $1 : \sqrt{2}^{12} = 1 : 1.0594631$, whereas the diameter increased in the ratio of $1 : \sqrt{2}^{24} = 1 : 1.0292857$. This theory gives, unfortunately, only approximate results, and, again, the length of the first pipe, the starting point for calculating the others, must be found empirically. What led the writer first into error as to the true value of this theory, which is very interesting for its origin and the time at which it was propounded, was that at that time he was wholly ignorant of the influence of the partial closing of the tubes caused by the way in which the air-columns of these *lus* are set in vibration, and that, undoubtedly, an imperfect test had accounted for the defect noted to-day.

In order to make this clearer the following empirical method was established; it will supply what is lacking in the above explanation.

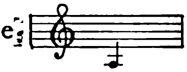
For example: let there be a tube which when fully open gives the sound  at the normal pitch. This sound produced by 976.5 single vibrations in a second, has a wave-length of

$$\frac{340}{976.5} = 348 \text{ mm.}$$

The tube being 19 mm. in diameter, three quarters of this diameter is 14.25 mm. This then is the amount by which the length of the wave must be reduced in order to have the length of the tube, hence

348
less 14.25
333.75 mm. = the length desired.

But it is found experimentally that, by the partial closing of the tube resulting from the adoption of any kind of mouthpiece, the intonation falls a full tone. This lowering can be determined in wave-length as follows:

390 mm., length of single wave of A
less 348 mm. " " " B
difference 42 mm., or the value of lowering caused by the partial closing of the tube which sounds the B, 60th degree of the scale of sounds. If it were desired to calculate the length to be given to a tube of the same diameter intended to give the , 46th degree of the same scale, the following method is used:

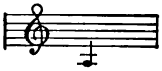
The length of the wave of B is................	348 mm.
The lowering caused by the partial closing is.....	42 "
Length of the A next below is.................	390 mm.
Double this length to bring it to the next octave below.	780 mm.

But, as has been said at the beginning of this paragraph, the influence of the partial closing is inversely proportioned to the length; hence, for a length double

390 mm., the effect will be one-half less and there must be taken from the total length............... 21 mm.

759 mm.

and, to withdraw also the influence of the diameter of the tube, 19 × ¾ =............................ 14 mm.

length of the tube sought for the  .... 745 mm.

which is confirmed by experience.

The complication of the phenomenon is great, and, it will be understood, its influence on the theoretical teaching of flute construction is enormous. It will be confessed that in spite of this importance the matter was neglected entirely in the author's *Elements d' acoustique !*[1]

18°. In trying the first ten tubes[2] as mentioned in §13 and in closing them to the same extent, deeper sounds are obtained by this partial covering than those of the *entirely* open tubes. But it is of the utmost importance to remark that, under these conditions, the intonations are alike from whatever side the air-column is set in vibration, that is to say whether it be at the larger or the smaller end. It is also to be remarked that in these air-columns, which are set in vibration by an opening in the direction of the axis, the lowering of the fundamental sound occurs also in the harmonics, so that their vibratory relation remains true; that is, it continues to be that of the open tubes, that of the natural series of whole numbers 1, 2, 3, 4, etc.

19°. The phenomenon of the harmonic resonance of the traverse flute is not exactly the same. The air-column of this last instrument is set in vibration through an opening made in the wall of the tube and smaller in diameter than the diameter of the air-column.

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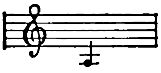
[1] This complication is increased further by the influence of the holes made in the sides of the bore. Thus the tube which gives the , the length of which has just been found to be 745 mm. will have its pitch sensibly lowered so soon as the lateral holes required for forming its scale have been bored. This influence is explained in this way: each of the openings made in the more or less thick walls of the tube adds somewhat to the length of the air-column which it contains.

[2] The reason why the tube *L* is excepted has been given.

The result of this peculiar position is that the lowering caused by the partial closing of the tube is greater in the fundamental sound than in its harmonics. The cavity which lies between the plug which closes the upper end of the tube and the opening through which the air-column is set in vibration is intended to correct this difference.[1] This cavity has no influence on the height of the fundamental sound; hence certain players who use the adjusting screw, which controls the movement of the plug, to tune the flute, do so wrongly. But if this cavity has no effect on the fundamental sound, it acts on the harmonics whose relation with the fundamental it corrects by lowering them.

As the air-column remains in communication at both ends with the surrounding air, it will be well to recall what was said in § 10: that a loop of vibration exists at each end of these open or partly closed tubes, no matter which of the sounds produced by the harmonic resonance may be uttered.

III. Closed or Stopped Tubes.

20°. By this term are known all those tubes which are closed at one end and are open at the other. In scientific terms they are: all those tubes which have a node of vibration at one end and a loop of vibration at the other. The vibratory motion in them is propagated from the outer to the inner end, from the bell to the mouthpiece, and not in the reverse direction as is generally believed and as is the case for open or partly stopped tubes. All the reed and all the mouthpiece instruments will be borne hereafter in this category.

The air-column contained in these tubes can be set in vibration in three different ways:

A by the breath directed against the edge of the open end, the other end being stopped.

B by a mouthpiece.

C by a reed.

Returning to the tubes, each of the ways of producing vibrations will be examined, noting that, whichever be the means used in the case of stopped tubes, the law of vibration does not change and that any change in the length of the tubes would cause no further modification in them.

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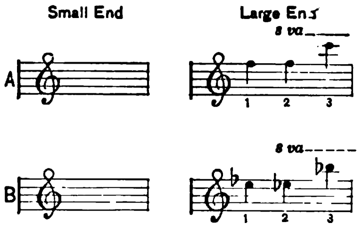
[1] **This difference is proportional to the difference between the diameter of the air-column and that of the side hole which acts as a mouth; thus it is greater in the flute than in the piccolo.**

A. Vibration by the Breath.

21°. This way of setting the air-chamber in vibration has been applied only in the *syringa*, commonly called the *pipes of Pan*. This instrument is made generally of cylindrical tubes of reed, stopped at one end, and set together side by side. According to the present theory, the length of each of these tubes is equal to that of half a single wave. Experience has shown that a correction is equally needed here. In fact it has been found that, to calculate the length of a cylindrical tube stopped at one end and intended to give a certain predetermined sound, *the length of the single wave of this sound must be reduced by a length equal to one-half the diameter of the tube.*[1] It is deemed useless to dwell longer on this mode of correction. What was said in connection with open tubes will suffice to show exactly the practical way of applying it.

22°. In the following table have been placed side by side the harmonic resonances obtained from each one of the eleven tubes by blowing alternately into the large and small ends, *the opposite end being stopped by the flat of the hand:*



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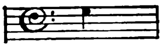
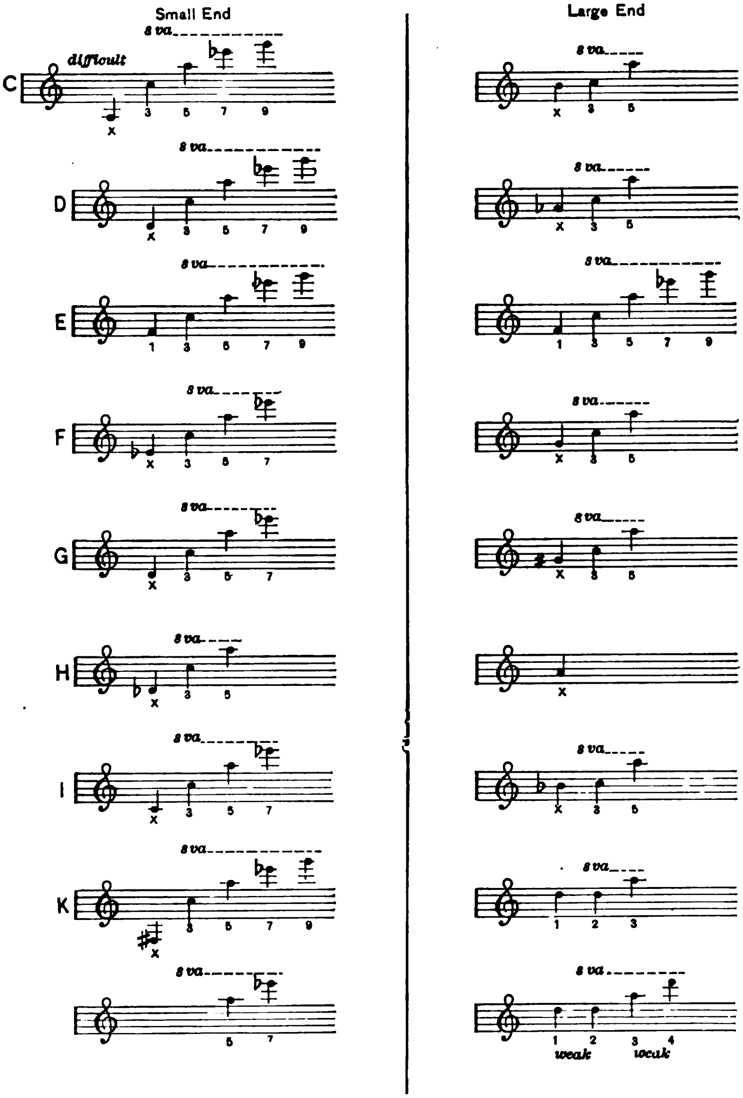
[1] It may be interesting to know that the maximum length of the tubes of which the fundamental sound can be produced by this way of blowing is very nearly the length of the  44th degree of the scale of sounds. The diameter has a certain influence on the production of the fundamental sound. If the diameter were very narrow, the tube would give harmonic 3 instead of the fundamental sound. It has been found experimentally that for a tube, vibrating under good conditions, to produce its fundamental sound, the diameter must be $\frac{1}{20}$ of its length.

23°. Trying each of the tubes separately it is found :

(*a*) That A and B cannot be made to vibrate by the small end, as A has no opening and that of B is too small. Set in vibration from the large end these same air-columns have a harmonic resonance exactly like that of the open tubes, *in spite of the fact that they are stopped.* This fact is in opposition to the existing theory as to the laws of vibration of air-columns.



(*b*) That E, the cylindrical tube, is the only one whose air-column vibrates in conformity with the laws of existing theory. The length of this tube giving the fundamental sound F, 54th degree of the scale of sounds, is equal to that of a single half-wave corrected as indicated in § 21, and its harmonics follow the series of odd numbers, 1, 3, 5, 7, etc.

(*c*) That the tube *H*, when the breath is applied at the large end gives only the fundamental sound, and that with a certain difficulty, on account of the exaggerated size of this diameter.

(*d*) That the tubes *C*, *D*, *F*, *G* (and this is a point of prime importance as it leads to the determination of the conditions needed by a stopped tube to acquire the harmonic resonance of an open tube) continue to preserve *approximately*[1] the odd-numbered harmonics of the cylindrical tube, no matter from which end they are set in vibration, while the fundamental sound rises or falls appreciably according as the breath is applied at the large or the small end. This deviation from the fundamental sound F of the cylindrical tube is due to a slackening or a hastening of the vibratory motion; it can be stated in terms of an equal number of vibrations which generates, therefore, in the same tube, a larger interval downward than it does upward. Furthermore the intonation of the sounds marked × is only approximate.

(*e*) That when the breath is applied to the large end of the tubes *C*, *I*, they have a resonance which approaches that of the open tubes.

(*f*) That, the tube *K* possessing the harmonic resonance of an open tube, it may be concluded that, for a tube of trunco-conical form to sound the octave, *the diameter of the open end must be at least four times that of the stopped end.*

To sum up what precedes: the conical tube closed at the vertex resounds like an open tube of the same length, and its resonance causes the harmonics to be heard successively in the natural order of the numbers 1, 2, 3, 4, etc. Within limits, the trunco-conical tube acts like the conical tube, but its pitch, compared with that of the open tube, becomes lower in proportion to the diameter of the truncated part, where the tube is stopped. An examination of the table, § 22, shows that this lowering is a minor third when compared with the intonation of the *wholly open* tube. It is needless to say that this lowering, which is a tone and a half for this small length, becomes less when a larger tube is used.

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[1] The harmonics rise or fall with the fundamental sound; it is stated that they stand *approximately* in unison with the odd-numbered harmonics of the cylindrical tube, because the variations in these sounds are much less marked than that noted in the fundamentals (see § 28, *b*).

The question, why a conical tube closed at the vertex of the cone resounds like an open tube, deserves careful consideration. One would be led to believe, at first glance, in the influence of the mass of air contained in the tube. This is not so. It is known that the volume of air contained in a cylindrical tube is four times as great as that contained in a conical tube of the same length and having the same diameter at the base.

Furthermore, if the mass of the air entered the question, the influence of the diameter would be much greater than that stated in §§ 11 and 12. The fact that the pitch of the cylindrical tube drops a full octave by the closing of one of its ends (§ 22) leaves it to be supposed that the phenomenon of the conical or trunco-conical tube, of given proportions, resounding like an open tube, is due to the reflexion of the vibratory motion, and that it is more rapid against the oblique sides of these trunco-conical tubes than against the bottom or stopper of the cylindrical tubes.

B. VIBRATION BY MEANS OF A MOUTHPIECE.

24°. If the ends of any one of the tubes be struck against the flat of the hand, the resulting fundamental sound, although very feeble, is sufficiently perceptible to allow noting that its pitch is the same as that of the sound obtained from the same tube when it is set in vibration by the breath *applied at the other end.* All the fundamental sounds of the table, § 22, are thus obtained, excepting naturally from these experiments the tubes *A* and *B*, the structure of which does not permit this form of vibration. It is well to note, however, that, as the pressure on the air-column thus obtained can only be uniform, it goes without saying that only one sound, the fundamental, can be obtained.

Hence, the excitation of the vibratory motion by striking the hand against one of the open ends of the tube is equivalent to closing this end completely, and this action does close the tube absolutely.

25°. If this means of setting the air-column in vibration be replaced by the one which consists in resting the same orifice against the lips, there is obtained a sound the same as the one given by the tube when the vibratory motion is obtained by the breath applied to the opposite end, and it is in this way that the air column of all the instruments used in the orchestra are set in vibration: cornets, bugles, horns, trombones, basses, etc. The harmonic resonances noted in the table, §22, remain absolutely the same, observing however that the division of the air-column which can be realized by the breath is not obtainable by the lips, because the latter cannot vibrate fast enough to secure movements synchronous with those which would follow from the division of the air-column caused by the production of harmonics in such short tubes. On the other hand, the air directed against one of the orifices of the tube has not sufficient energy to impart the vibratory motion to air-columns of too great length. (See note to §21.)

An inspection of the above-mentioned table shows that the only tubes suitable for the construction of our mouthpiece instruments are those of the types *B*, *K*, *L*. But, without hurting their lips, players could not set an air-column in vibration by applying the lips directly to the tube which contains it. This is why an intermediate apparatus, called a *mouthpiece*, is used; it is, in a word, only a prolongation of the tube ending in a cup around which is worked a comparatively wide flange against which the performer places his lips. The shape of the cup has necessarily a certain influence on the tone color, and on the facility with which the air-column is set in vibration. The mouthpiece must be arranged conveniently and according to rules taught by practice or experience.

A node of vibration, with continual changes of density and pressure is found at the mouthpiece of all mouthpiece instruments; a loop of vibration, with maximum velocities of motion is found at the bell. To blow into instruments is an improper expression; players only blow into certain reed instruments and even then the term is rigorously exact for the cremonas only (Nos. 610 *et seq.* of the catalogue) or for instruments with an air reservoir. The air is a motive force used to put the air-column in motion, either directly (as in the flutes), or through the medium of the lips (mouthpiece instruments), or .through the medium of the apparatus called *reed* (clarinettes, oboes, bassoons, etc.).

26°. Hence, all the mouthpiece instruments are tubes stopped at the mouthpiece end. They possess, by reason of suitably established proportions of their air-columns, the complete harmonic resonance of the tubes *B*, *K*, *L*.

27°. Experience shows that tubes of trunco-conical form are not the ones most to be recommended for mouthpiece instruments. The tone-quality resulting from the vibration of this form of air-column is harsh and wild; it is the characteristic tone-quality of primitive instruments, made of horns of animals, and even also that of periods when the maker's art had already made some advance, as the Danish *Lur* of bronze. (See No. 1,156 of the Museum of the Conservatory.)

The progressive enlargement of the air-column must be made along certain curves, sought even in these later days by trial, which are associated in certain cases with a longer or shorter cylindrical tube.

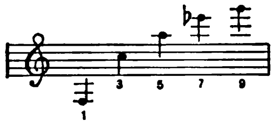
Thanks to this association being allowable, the shape of the air-column of mouthpiece instruments can be varied infinitely, and thus all the varieties of tone quality indispensable for the orchestra can be had, while the resonant qualities of trunco-conical tubes relatively to the just ratio of the harmonics with the fundamental sound are preserved.

28°. Numerous trials allow the establishment of the following facts, which do not differ from those already noted in §22 and 23:

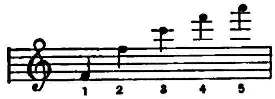
(*a*) If a mouthpiece be applied to a cylindrical tube, the air-column vibrates like a stopped tube and only the odd-numbered harmonics are heard; furthermore the sound lacks fulness.

(*b*) So soon as the lower part of the tube is expanded and receives a conical form, the resonance improves, the fundamental sound rises as do also the harmonics, the latter approaching gradually, as the cone advances, the ratio given by the series of figures 1, 2, 3, 4, etc. This phenomenon is noticed even when the tube is enlarged for only a small part of its length at the end opposite the mouthpiece. It appears first in the upper harmonics, and reaches its finality when the enlargement of the tube is obtained under the proportions given in the following paragraph. The annexed table will make the matter clearer. It shows the harmonic resonance of any two tubes of the same length, in F, the one cylindrical, resounding like a stopped tube, the other conical, resounding like an open tube.[1]

Cylindrical tube,



Conical tube,



The proper enlargement being applied to a cylindrical tube causes sound 1 to rise to its octave which then becomes sound 1 of the conical tube; sound 3 becomes sound 2; sound 5 becomes sound 3; sound 7 becomes sound 4; sound 9 becomes sound 5, and so on. It can be conceived that the slightest expansion given to the tube may produce the small approach required for the high sounds, but that a much more marked enlargement is needed to make the low sounds rise by the desired amount. The intervals become more and more contracted as the enlargement of the lower end of the tube progresses, and when this reaches the proportion given in the next paragraph, the twelfth 1 : 3 becomes the octave 1 : 2; the major sixth 3 : 5 becomes the fifth 2 : 3; the minor fifth 5 : 7 becomes the fourth 3 : 4; the large major third 7 : 9 becomes the major-third 4 : 5, etc. It will be noticed that the difference in the intervals given by the succession of the harmonics *in the two kinds of tubes* becomes smaller and smaller, and continuing onward they might even become confounded within a very small difference. This phenomenon brings us very close to the law which governs the vibration of these air-columns. If this law cannot yet be stated in precise terms, the observed phenomena are sufficiently clear to show even now the reason why a tube may be cylindrical for a part of its length, starting from the mouthpiece, and then must become wider as the opposite end, generally called the bell, is neared.

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[1] This scale of a cylindrical tube of which the air-column is set in vibration by a mouthpiece is only hypothetical. A cylindrical tube of sufficiently small diameter to be set in vibration by the lips, and, on the other hand, sufficiently long to give theoretically this low F, would only speak very imperfectly in practice; the low sounds would not be produced.

(*c*) That the high harmonics may be in exact relation to each other without their being so to the fundamental sound (trumpet, trombone). Experience has shown that it is indispensable, in order to have the relation of an octave between the fundamental sound and sound 2, that the gradual enlargement of the air-column begin, at the least, at the middle of its length, and that the minimum ratio of the diameters of the ends of the tube be as 1 to 4. The sudden expansion called the *bell* is not included in the determination of the ratio between the extreme diameters.[1] This enlargement is a mere question of shape, of style. It is very differently made in different countries, and in some, Germany for example, it is omitted altogether, without the manufacture of the mouthpiece instruments being in any way inferior on this account.

Trumpets and trombones, as already said, do not give the fundamental sound, or at least they give it with difficulty, and its relation is not true; it is generally too low as compared with sound 2 at which the scale of these instruments begins. This defect is owing to the lower part of their air-column which only begins to expand at the last third of its length. They might be called *incomplete instruments*.

(*d*) That the brilliant tone quality (trumpet and trombone) is favored by the use of narrow tubes and that, on the other hand, the smooth unctuous tone quality characteristic of the basses is due solely to the broadness of their air-column. In these instruments, which will be called *complete*,[2] the expansion of the tube begins immediately back of the mouthpiece; in some of them the ratio between the two extreme diameters is at times 1 to 20.

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[1] It appears from experiments made by M. Mahillon since his pamphlet was published, that the size of the bell has some influence on the sound quality. This influence is especially marked in the case of the horn of which the bell is very largely developed, and of which the peculiar, *sui generis*, sound quality may be mainly attributed to this part of the instrument. M. Mahillon noticed that as the bell was more and more cut off the soft sound quality of the horn became lost and approached the brilliant sound quality characteristic of the trombone and the trumpet.

By reason of the sharp enlargement of its bell the pitch of the horn does not change sensibly in spite of this shortening of the air-column and the high harmonics are obtained more easily. This last phenomenon is explained, in M. Mahillon's opinion, by the reduced friction of the air against the wall of the tube.

29°. Variety of tone qualities follows from the many proportions which can be given to the air-column. In certain cases, it was seen in the trumpet and trombone, technical reasons make it necessary to utilize the cylindrical tube prolonged by another tube of which the diameter becomes gradually larger. But it is wrong to qualify as "conical" this shape which is given to the lower part of the air-column. The cone joined to the cylinder would not form a regular air-column, the division of the latter into aliquot parts, absolutely necessary for the production of harmonics, would be impossible and consequently the harmonics would be false with each other and with the fundamental sound. Hence the prime necessity that the tube should expand smoothly instead of being formed with walls of broken lines. This *sine qua non* condition is reached by using, as already said in §27, curved lines which continue the cylindrical part uninterruptedly, thus forming tubes of which the forms are those of surfaces of revolution generated by these curves when made to revolve about the axes of the tubes. The determination of these curves, their equations and their forms lie beyond the scope of this paper. They will form the object of a special article. Moreover, the subject is interesting only to instrument makers.

C. VIBRATION BY MEANS OF A REED.

30°. The resonance of tubes set in motion by this medium is the same as that obtained by producing the vibration with a mouthpiece. The tube, instead of being closed at its upper end by a mouthpiece, is now closed by a reed, and it is at the end of the latter that the node of vibration is found, the loop of vibration being at the other end, the bell. The reed may be single or double, it matters little which, the result is the same if the lowering of the air-column caused by the reed be the same. (See further on, §32.)

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[2] The distinction between these two kinds of instruments is made in Germany. Zamminer (*die Musik und die musikalischen Instrumenten*, Giessen, 1855) calls them *Halbinstrumenten* and *Ganzinstrumenten*. There is in the orchestra but one complete mouthpiece instrument, that is, one whose scale begins with sound 1. It is the tuba or bass in B*b*; it is so made because it replaced the ophiclied whose scale utilized the first octave. It will be added that this exception is not to be recommended, seeing that the present methods of instrument-making are wholly unequal to intercalating perfectly accurately the eleven chromatic degrees in the octave between sound 1 and sound 2.

The resonant types of the oboes, English horns, bassoons, double bassoons, saxophones, are the trunco-conical tubes *B*, *K*. The cylindrical tube *E* is the type of the clarinet.

31°. This phenomenon explains the doubling of the fundamental sounds at the octave or at the twelfth above by the mere increase of pressure on the reed. From it flows evidently the necessity that all instruments with side holes—the successive opening of which has for its object the production of consecutive degrees of the scale—should preserve very exactly, from the first lateral hole next the reed, either the cone with the ratio of the diameter 1 : 4 for tubes intended to sound the octave above the fundamental, or the cylinder for those intended to sound the twelfth.

The question is often asked, why, if the shape of the reed being single or double is without influence, the double reed is used generally with trunco-conical tubes, and the single reed with cylindrical tubes? A moment's reflection gives the answer to the question. The single reed is always cut out from a tube having itself a certain diameter; the necessity of giving to the tube, at the position of the side hole nearest the reed, a diameter four times that of the tube in which the tongue of the reed is taken, evidently makes it obligatory to give the air-column a very marked conical shape, which can only be accomplished by the machinery which modern instrument-making has at its disposal. The saxophone is an example. Hence, this reed was suited exclusively to cylindrical tubes.

On the other hand, the slips of the double reed are attached very easily to a little conical tube of which the upper end has a very small section. The difficulty of giving the air-column of this tube the proportion 1 :.4 desired was not great for the means which the old makers had at their disposal. Hence, the double reed found its place necessarily when associated with the conical tube. Only exceptionally was it associated with cylindrical tubes (cremonas, cervelas).

32°. The reed not only closes the tube but, by the resistance it offers to the breath, it lowers, in proportion to its elasticity, the pitch of the air-column.[1] It acts, furthermore, like the partial closing mentioned in § 17. What completes the comparison is that its influence is also: *inversely proportional to the length of the air-column with which it is associated.*[2]

The slips of reed used in making the reeds of breath instruments are extremely sensitive to the pressure of the breath; very great differences of pitch can be obtained by varying the pressure. The flexibility of these reeds is so great that they can set in vibration air-columns of very different lengths. It is this property of the slips of reed which allows the numerous shortenings of the air-columns by the side holes.

Metallic reeds do not possess this property. Their invariable degree of elasticity causes them to give a single sound, and when they are associated with tubes, they demand the use of air-columns in harmony with them within very narrow limits. It is enough to break the proportion to prevent the vibratory motion of the reed (Chinese *cheng*, No. 137; Siamese *khĕn* No. 138 of the catalogue), or, at the least to disturb its regularity, and to give rise to intonations which are painful to the ear.[3]

33°. This peculiarity of the reed to have, as it were, an intonation of its own causes the tube to which it is applied to act merely as a reverberator or intensifier while following however the laws of the resonance of tubes. It also explains the fact that the intonation which follows from the association of the reed with the tube, instead of falling with increase of diameter, as is the case with tubes in which the air is set in motion without any intermediary, or at the least by the intervention of the breath or the mouthpiece, follows a contrary law ; it falls with diminution of the diameter. Thus, it has been noticed that a cylindrical tube 414 mm. (16 ⅓ inches) long and 6 mm. (¼ inch) in diameter gives, with an *arghoul*[1] reed, a sound at the in diameter set in vibration with the same reed gives a sound a minor fifth higher.

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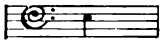
[1] The lowering influence of the reed on an air-column can be shown easily. Let a clarinet mouthpiece and its reed be taken; the pitch obtained by the use of the reed will be about a tone lower than that which would be obtained by directing the breath against the lower opening opposite to the position of the reed. The pressure on the reed must not be exaggerated in the first case; in the second, it is indispensable to bring the reed tight against the table so that the stoppage of the tube be complete.

[2] It follows from this fact that for instruments provided with side holes the lowering of intonation due to the influence of a partial closing of the tube or of the application of a reed, is greater on the holes near the apparatus used to produce the vibratory motion than on those farther away. The action of the lips is compared generally with that of the reed. This comparison is not correct. It has been seen that the air-column of tube *E*, set in motion by the breath (§ 23, *b*), gives exactly the same sound F as does this same air-column when it is set in vibratory motion by means of the lips placed against the open end (§ 25).

[3] Since the above was printed, M. Mahillon has come into possession of a sort of Siamese *chalumean*, composed of a long cylindrical tube pierced with several lateral holes. Its air-column is set in vibration by means of a metallic reed glued over a rectangular opening at the other end of the tube, which gives to the whole the appearance of a traverse flute. In spite of the metallic reed, this *chalumean* produces sounds which are higher as the tube is shortened by opening the holes on the side. Hence it follows that when the metallic reed is sufficiently thin it may be substituted in certain cases for the cane reed, of which it acquires the flexibility and properties.

pitch of , while a tube of the same length and 12 mm.

[1] The *arghoul* is a very ancient Egyptian instrument (See *Catalogue du Musée*, Nos. 113, 114) and very certainly the primordial type of the association of the vibrating reed with the cylindrical tube.

ON THE FREEZING-POINTS OF AQUEOUS SOLUTIONS OF NON-ELECTROLYTES. II.

By E. H. Loomis.

IN a former paper on the same subject[1] it has been shown that the freezing-points of equimolecular solutions of a large number of non-electrolytes in extreme dilution are the same. Thus it was found that the solutions whose strength is $\frac{1}{100}$ gram-molecule per liter of the solution all freeze at $-0^\circ.0186$ C. This means that the van't Hoff constant is valid for all such solutions and that its value is 1.86. There were three noticeable exceptions, methyl alcohol, ethyl alcohol, and ether, which gave the respective values, 1.82, 1.84 and 1.50. With the desire to make the examination of the problem as complete as possible and with the hope that additional experimental data would perhaps enable us to account for the very important exceptions which these three substances exhibited the work was extended. The results form the material of the present paper.

It is helpful at the outset to examine in some detail the behavior of the thermometer. This thermometer has now been in use for seven years. Its zero-point continues to rise. When it left the Reichsanstalt where it was corrected, its zero was + 0.015. It is now + 0.057. During the last period of observation (January–March, 1900) it has risen $0.^\circ0018$ C., as appears by an examination of the successive zero-points which were observed in this period and which are presented in the following table.

These zero-points are each the average of three or four separate determinations which were made in close succession in the early part of the day on which the freezing-points of the solutions were observed.

The old questions suggest themselves:

1. How well do these separate determinations agree among themselves?

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[1] Physical Review, 1899, IX., No. 5, p. 257.

TABLE I.

1 Date.	2 Observed Zero.	3 Barometer.	4 Room-Temperature.	5 Zero Cor't to 0°C. and 760 mm.	6 Maximum Variation.	7 Depressions Observed on the Given Zero.
1900	°		°			
Jan. 27	+0.0555	763.3	2.0	0.0542	4 in 4 obs.	Salicine.
" 29	0.0545	750.6	2.0	0.0553	1 in 3	Urea.
" 30	0.0556	755.9	2.0	0.0537	2 in 3	Milk-sugar.
" 31	0.0552	748.3	3.0	0.0570	4 in 3	Phenol.
Feb. 1	0.0558	754.4	2.0	0.0559	4 in 3	Levulose and dulcite.
" 2	0.0562	759.7	2.0	0.0555	2 in 3	Acetamid and resorcin.
" 6	0.0593	773.7	2.0	0.0562	1 in 3	Maltose.
" 19	0.0562	755.9	2.0	0.0555	5 in 3	Hydroquinone.
" 20	0.0578	766.1	2.0	0.0560	3 in 3	Pyrocatechin.
" 26	0.0566	756.7	2.0	0.0564	7 in 3	Pyrogallol.
Mar. 12	0.0573	760.5	2.0	0.0564	5 in 3	Benzamid.
" 16	0.0556	744.7	2.0	0.0573	3 in 3	Various controls.

2. How constant does the zero-point of the thermometer remain during a long period of use?

The first question may be answered by reference to the facts given in column 6 of the table, where the difference between the highest and lowest values of the observed zero-point is given for each day of observations. Thus on January 27th, the observed zero was + 0°.0555, and in column 6 it is indicated that this zero was the average value of four separate determinations which differed among themselves by 0°.0004 C. The greatest variation appeared in the zero-point which was observed February 26th, where it reached the amount 0°.0007 C. in three determinations; while the least variation appeared in the zero-points for January 29th and February 6th when it is only 0°.0001 C. in three determinations. The same satisfactory agreement between the individual observations which make

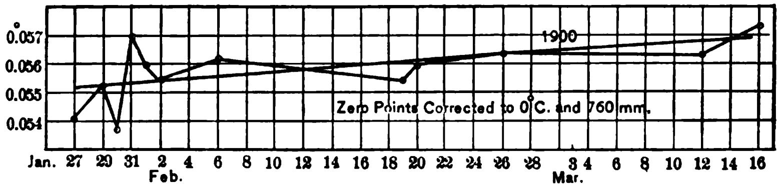

Fig. 1.

up a series whose average value is taken as the desired zero point appears also when we examine the observations on the freezing-points of the various solutions. Without going into details a fair idea of the actual fact may be obtained from the following general statement.

For all the solutions of the strength $\frac{1}{100}$ gram-molecule per liter, the average variation is 0°.0002 C. in three observations. In one instance it was as much as 0°.0006 C. (maltose, February 27th), while on the other hand there was no variation at all in three series, namely, those for milk sugar, levulose and acetamid. Of the more concentrated solutions, let us take those whose strength is $\frac{1}{10}$ gram-molecule. In the observations on their freezing-points, the average variation was 0°.0003 C. The least constant series (hydroquinone, February 19th), showed a variation of 0°.0010 C. in two observations, while again three entire series showed no variation whatever.

The second question,—how nearly constant does the zero-point of the thermometer remain during a long period of use may be answered by reference to the facts in column (5), or by an examination of the diagram immediately under the table. The twelve zero-points here recorded show an apparent variation of 0°.0036 C., the most of which comes out in the first three of the series. Here, as in the former series, there is the same unmistakable *rise* of the zero-point. Assuming that the actual rate at which this elevation of the zero-point went on was uniform throughout the period, we find that the total rise was 0°.0018 C. The dotted line in the diagram represents this uniform rise of the zero-point. It must be remarked that the present series of zero-points is not so satisfactory as those of the two previous years. While the total variation which the series exhibits is by no means great, the fact that it is not distributed over the entire series but is crowded into the first three days of observations is very hard to explain. It does not, for example, seem possible for us to explain this very sudden change in the observed zero-point which appeared between January 30th and January 31st, by simply assuming that the observations were here attended by very unusual experimental errors. Such an assumption would require us to believe that the observed zero-point on January 30th was 0°.0015 C. too low and on the following day as much too high. If this were so, then it would follow almost certainly that the solutions whose depressions were measured in these days would exhibit abnormal results. Thus the depressions for milk sugar, measured on January 30th would have been abnormally small; while those of phenol measured on the following day would have been abnormally great. However, an examination of the results for these two substances furnishes us with no evidence that such was the case.

Does the thermometer then really change its zero-point suddenly? There seems to be no escape from this disagreeable conclusion. Still, such sudden changes are at the worst very rare, and have little influence on the general character of the results. On only one occasion have I detected such a sudden change by direct observation. On February 26, 1898, a series of observations on the zero-point of the thermometer, begun in the morning, was interrupted and finished in the afternoon. The three individual observations of the morning agreed within 0°.0005 C., and gave the average value for the zero-point, + 0°.0538. The first observation in the afternoon series gave + *0°.0521*. I was so amazed at the result that I at once assumed that some impurity had fallen into the water, presumably a bit of salt, and accordingly replaced the water with a fresh portion before going on with the series. The two following observations, however, were + 0°.0520 and + 0°.0519 respectively, thus agreeing with the one already made. Was it possible that the zero-point had fallen 0°.0020 C.? I tried to avoid this conclusion by trying to believe that the scale of the thermometer had been displaced by the jarring. (The thermometer is of the enclosed type with graduations on milk glass.) I found, however, that no amount of jarring resulted in any measurable displacement of the scale. For the present therefore it seems necessary to admit that the zero-point of the thermometer may suddenly change. Before finally accepting this disagreeable conclusion I propose to test the matter by a series of experiments made especially for the purpose. I may be permitted to say here that a full knowledge of all the facts which have come to light during the long period that the author has been occupied with the present method and which he has aimed to submit to the public with as little bias as possible, has always deterred him from making any claims in regard to the accuracy of the method, much more from fixing any numerical value to the probable experimental error. I may say, however, that this error is certainly not as low as some experimenters have claimed for their methods. In some cases this assumed error has been fixed as low as 0°.0001 C. Suffice it to say that when this limit of error has been actually attained, we may reasonably expect an experimental answer to a number of important questions which as yet are wholly beyond our reach.

The present series of observations includes the compounds in the following table :

TABLE II.

1 Compound.	2 Formula.	3 Grams per Liter of Solution.	4 Gram-Mol. per Liter. (*m*)	5 Sp. gr. ($\frac{18}{4}$) of Solution in (4)	6 Source of Material.
Milk sugar.	$C_{12}H_{22}O_{11}$	68.44	0.20	1.0256	Merck & Co.
Maltose.	$C_{12}H_{22}O_{11}$	68.44	0.20	1.0250	Kahlbaum.
Levulose.	$C_6H_{12}O_6$	36.02	0.20	1.0127	Kahlbaum.
Dulcite.	$C_6H_8(OH)_6$	18.21	0.10	1.0047	Kahlbaum.
Acetamid.	$C_2H_3ONH_2$	11.82	0.20	0.9995	Kahlbaum.
Salicine.	$C_{13}H_{18}O_7$	22.89	0.08	1.0054	Merck & Co.

Together with other usual data the table also gives the specific gravity $\left(\frac{18^\circ}{4^\circ}\right)$ of the various solutions whose strength is 0.10 and 0.20 gram-molecules per liter respectively. The specific gravities were made with a Mohr balance, and are only accurate to within ± 0.0002.

The detailed observations of the freezing points of the various solution will now be submitted.

MILK SUGAR. JAN. 30, 1900.

The original product was from Merck & Co. After twice recrystallizing it was powdered and exposed to $CaCl_2$ for many days at room temperature. When so treated its composition is $C_{12}H_{22}O_{11}$, H_2O. The solution $m = 0.20$ was made by direct weighing. In the table of results m denotes the number of gram-molecules of the dissolved substance per liter of the *solution* and $\triangle$ the depression of the freezing-point. Thus $\frac{\Delta}{m}$ denotes the *molecular depression* of the freezing-point. *P* denotes the number of grams of the substance which a given solution contains per 1,000 grams of water, which is easily calculable when the specific gravity of the given solution is known. This is nearly enough known for any of the dilute solutions when we know the specific gravity of the most concentrated solutions and assume that for the more dilute solutions the specific gravity decreases linearly with the decrease of concentration. By dividing *P* by the molecular weight of the compound we get the value of m' which is the number of gram-molecules of the substance per 1,000 grams of water. The formula $\frac{\Delta}{m'}$ is then what I shall call the *corrected value of the molecular depression.*

Milk Sugar.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0°.0186	1.86	3.432	0.01	1.86
0.02	0.0372	1.86	6.878	0.0201	1.85
0.05	0.0945	1.89	17.313	0.0506	1.87
0.10	0.1907	1.907	34.994	0.1023	1.864
0.20	0.3919	1.959	71.503	0.2089	1.876

It appears that the molecular depression $\frac{\Delta}{m}$ increases with the increase in the strength of the solution, and by assuming experimental errors of — 0°.0002 for the observed depression at $m = 0.02$

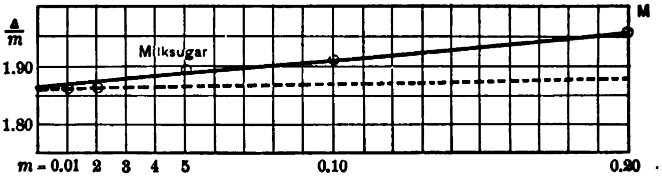

Fig. 2.

and $m = 0.10$, and an error of + 0°.0003 for the solution $m = 0.05$, this increase in the value of the molecular depression may be said to be *uniform*, as is indicated by the straight line in the diagram.

By extrapolation beyond $m = 0.01$, the value of the molecular depression in extreme dilution is found to be 1.86. It rises to 1.96 at $m = 0.20$. It is to be observed that the corrected values for the molecular depressions, as given by $\frac{\Delta}{m'}$, show the very slight uniform increase from 1.86 to 1.88. These values are represented by the dotted line.

MALTOSE, FEB. 6, 1900.

The original product from Kahlbaum was twice recrystallized from 80 per cent. ethyl alcohol according to the practice of Soxhlet.[1]

The resulting product was perfectly white and yielded a colorless solution in water. According to Soxhlet the maltose so prepared should be made up of large, well-formed crystals. A dozen or more attempts to obtain such crystals, however, resulted in failure. In each attempt the crystals obtained were too small to be seen with the unaided eye. The product resembled pieces of ordinary cooking starch. Under the microscope, however, the beautiful crystalline character of the maltose could be seen. The maltose was dried at room-temperature over H_2SO_4 to constant weight. When maltose is so handled its constitution is given by the formula $C_{12}H_{22}O_{11}, H_2O$. The solution $m = 0.20$ was made up by direct weight.

Maltose.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0°.0193	1.93	3.431	0.01	1.93
0.02	0.0378	1.89	6.879	0.0201	1.88
0.03	0.0560	1.87	10.350	0.0302	1.85
0.05	0.0946	1.89	17.316	0.0506	1.87
0.10	0.1919	1.919	35.004	0.1023	1.876
0.20	0.3946	1 973	71.548	0.2091	1.887

Again it appears that the molecular depression increases uniformly with the increase in the strength of solution. This conclusion requires the admission, however, of considerable experimental errors, + 0°.0006 C. at $m = 0.01$, + 0°.0003 at $m = 0.02$ and − 0°.0005 at $m = 0.05$. The straight line in the diagram represents this uniform rise in the values of the molecular depression. It must be remarked that in this case a curved line with a rather abrupt minimum at

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[1] Soxhlet, Jour. Prak. Chem., 1880, XXI., p. 274.

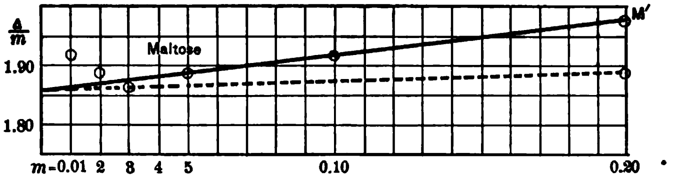

Fig. 3.

$m = 0.05$ would better represent the results. This matter will receive attention in the general discussion of the results.

Here, as in the case of milk sugar, the value of the molecular depression in extreme dilution is 1.86 increasing to 1.97 at $m = 0.20$. The values of the molecular depression obtained by the formula $\frac{\Delta}{m'}$ shows a slight uniform rise from 1.86 to 1.89 as is shown in the diagram by the dotted line.

Levulose. Feb. 1, 1900.

The levulose was from Kahlbaum and bore his label, "Lävulose aus Inulin." It was a mass of large and beautifully formed crystals, which were transparent and exhibited the smallest trace of straw-color. These crystals were permanent in the air, they showed no trace of being hygroscopic and gave a perfectly colorless solution in water. I wish here to express my personal indebtedness to Mr. Kahlbaum for his fidelity to the cause of pure science in the production of such difficult and little used preparations, many of which have been of incalculable value to me in my work. The product was powdered and dried over H_2SO_4. The solution, $m = 1$, was made by direct weight, assuming the formula for levulose crystals, $C_6H_{12}O_6$.

Levulose.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0°.0186	1.86	1.804	0.01	1.86
0.02	0.0375	1.88	3.613	0.0201	1.87
0.05	0.0939	1.88	9.062	0.0503	1.87
0.10	0.1890	1.890	18.235	0.1013	1.867
0.20	0.3836	1.918	36.918	0.2050	1.871

Here again the results show a uniform increase in the molecular depression, beginning with the value 1.86 in extreme dilution and rising to the value 1.92 at $m = 0.20$. The formula $\frac{\Delta}{m'}$ shows the very slight increase from 1.86 to 1.87. It is noticeable that these conclusions require the assumption of no appreciable experimental errors in any of the observations.

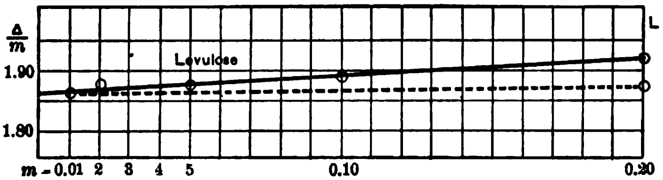

Fig. 4.

DULCITE. FEB. 1, 1900.

The original product was from Kahlbaum. It was white and well crystallized. Exposure over H_2SO_4 resulted in no sensible loss of weight. The solution $m = 0.10$ was made by direct weight. The limits of solubility do not permit the solution $m = 0.20$.

Dulcite.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	0°.0185	1.85	1.825	0.01	1.85
0.02	0.0377	1.88	3.654	0.0201	1.88
0.05	0.0927	1.86	8.969	0.0504	1.84
0.10	0.1877	1.877	18.460	0.1014	1.852

The results show a molecular depression of 1.85 in extreme dilution and a uniform rise to 1.88 at $m = 1.10$. This conclusion is represented by the straight line in the diagram and requires the admission of experimental errors of — 0°.0001 C., + 0°.0004 C., and

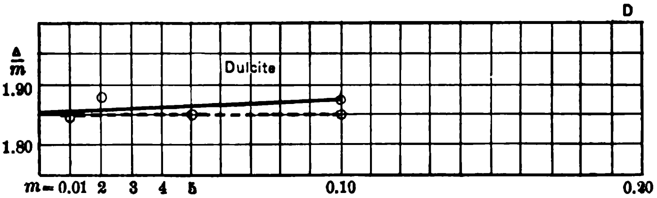

Fig. 5.

— 0°.0003 C. in the observations, $m = 0.01$, $m = 0.02$ and $m = 0.05$ respectively. The molecular depression calculated with the formula $\frac{\Delta}{m'}$ gives the constant value 1.85 for all concentrations.

ACETAMID. FEB. 2, 1900.

The original product from Kahlbaum was redistilled. The distillate was allowed to crystallize slowly from fusion. After about one-half of the fused product had thus crystallized the remaining liquid was poured off and the crystalline residue dried over H_2SO_4 for some months. It needs to be said that the product still retains a slight odor. The solution $m = 1.0$ was made by direct weight, due attention being given to the fact that acetamid is hygroscopic. The specific gravity of the solution $m = 1$ is 1.0027 at 18° C.

Acetamid.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	$\overset{\circ}{0}.0183$	1.83	0.591	0.01	1.83
0.02	0.0362	1.81	1.183	0.02	1.81
0.05	0.0917	1.83	2.962	0.0502	1.82
0.10	0.1835	1.84	5.948	0.1007	1.83
0.20	0.3684	1.84	11.968	0.2026	1.82
1.00	1.878	1.88	61.29	1.0375	1.81

It appears again that the molecular depression increases uniformly with the increase of the solution's strength throughout the entire region from $m = 0.01$ to $m = 1$, providing we assume experimental errors of — 0°.0004, + 0°.0002 and + 0°.0004 in the observations at $m = 0.02$, 0.05 and $m = 0.20$ respectively. The molecular depression, however, in extreme dilution is *only 1.83*. It rises uniformly to 1.88 at $m = 1.0$. The use of the formula $\frac{\Delta}{m'}$ gives value

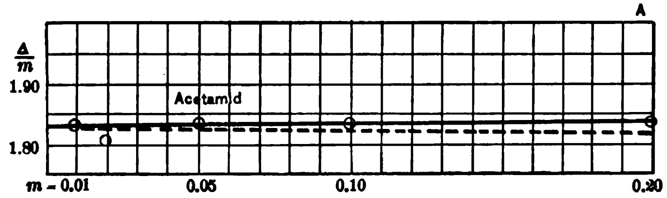

Fig. 6.

for the molecular depression which decrease uniformly from 1.83 to 1.81.

It needs to be remarked that the exceptional character of the molecular depression for this substance came to light in the work done upon it in the year 1899. The fear, however, that this might be due to some impurity in the acetamid or to lack of proper attention to the hygroscopic nature of the substance deterred me from publishing the results until the entire series could be repeated. The two series are identical within the limits of experimental error, and establish the exceptional character of acetamid.

SALICINE. JAN. 27, 1900.

The original product from Merck and Co. was twice recrystalized from dilute ethyl alcohol. It then yielded a colorless solution with water. After long exposure over H_2SO_4 it was made into the solution $m = 0.08$ by weight.

Salicine.

m	Δ	Δ/m	P	m'	Δ/m'
0.01	$0^\circ.0183$	1.83	2.870	0.01	1.83
0.02	0.0374	1.87	5.751	0.0201	1.86
0.05	0.0935	1.87	14.475	0.0506	1.85
0.08	0.1497	1.87	23.300	0.0814	1.84

Again the molecular depression shows a uniform increase from 1.86 in extreme dilution to 1.87 at $m = 0.08$. This conclusion

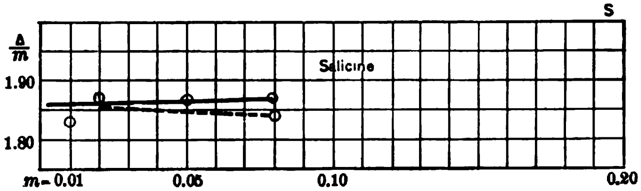

Fig. 7.

requires the admission of experimental errors of $-0^\circ.0002$, and $+0^\circ.0002$ at $m = 0.01$ and $m = 0.02$, respectively. The formula $\frac{\Delta}{m'}$ gives values for the molecular depression which exhibit a uniform decrease from 1.86 to 1.84. I wish to say that I have made many attempts to obtain new values for the molecular depression of urea, one of the three non-electrolytes examined in 1893. So far the results seem to show that this compound is unstable in aqueous solution. I shall resume work on this compound at the earliest opportunity and shall submit the results as soon as a definite conclusion is reached.

SUMMARY OF THE EXPERIMENTAL FACTS.

The experimental results submitted in this paper confirm the conclusions which were reached on the basis of the work already described in the former paper on the same subject: *Equi-molecular aqueous solutions of non-electrolytes in extreme dilution have the same freezing-points.*

By taking the results of the present paper together with these of the former paper we find that the following compounds in extreme aqueous dilution give 1.86 as the most probable value of their molecular depression:—*n*-propyl alcohol, *n*-butyl alcohol, amyl alcohol, acetone, glycerine, cane sugar, milk sugar, maltose, dextrose, levulose, mannite (1.85), dulcite (1.85), salicine, chloral hydrate and aniline. This indicates that the van't Hoff constant is valid for this large number of substances and that its value is 1.86–1.85.

The exceptions to this conclusion which were found in the former paper were presented by methyl alcohol, ethyl alcohol and ether. The present paper presents an additional exception in the case of acetamide, whose molecular depression, like those for the other exceptional cases, is abnormally low, namely 1.83.

2. Let us now examine the values of the molecular depression as given by the formula, $\frac{\Delta}{m}$, where m denotes the gram-molecules of the compound in 1,000 cc. of the solution.

The experimental results establish the following general statement: *For a given non-electrolyte the molecular depression* $\left(\frac{\Delta}{m}\right)$ *changes uniformly with the concentration of the solution.* Or by using the graphic method of expressing the results we may say that the "curves" which express the molecular depression as functions of the concentrations are straight lines. *The present experimental results do not indicate the slightest maximum or minimum values in* *the molecular depressions* within the region of concentration which has been examined. The only exception appears to be ethyl ether. It is necessary, however, to remark that recent experiments made on the evaporation of this compound from its aqueous solutions indicate that the exceptional values of its molecular depression were due to this cause.

It needs further to be remarked that in order to make maltose conform to this general statement of the experimental results, very unusual experimental errors must be assumed. Thus an error of $0^\circ.0006$ must be assumed at $m = 0.01$; otherwise a *minimum* value would come to light at $m = 0.03$. I am not satisfied that such an error actually appears in the experimental data, since a repeated observation at $m = 0.01$ gave the same high value. Since this compound is the only one out of eighteen compounds already examined which exhibits the smallest tendency to develop a minimum value of the molecular depression I am unwilling to look upon it as presenting a real exception to our general statement until further work is done upon it.

3. Let us next examine the values of the molecular depressions as calculated from the formula $\frac{\Delta}{m'}$ where m' denotes the strength of the solution in gram-molecules of the solute per *1,000 grams of water*. The quantity m' is easily found for any given value of m when the specific gravity of the solution is known. Obviously m' is greater than m, and the values of the molecular depression $\frac{\Delta}{m'}$ are therefore smaller than the molecular depressions $\frac{\Delta}{m}$. In solutions of extreme dilution where the volume of the solute is negligibly small compared with that of the water in the solution the values of m' and m are practically the same and so also $\frac{\Delta}{m'}$ and $\frac{\Delta}{m}$. As the solution becomes more concentrated the volume of the solute increases and the value of m' diverges more and more widely from that of m. The values of the molecular depression, $\frac{\Delta}{m'}$, may be summarized as follows :

(*a*) *The molecular depressions*, $\frac{\Delta}{m'}$, *remain constant for all the various concentrations of a given solution*, in the cases of methyl alcohol, (1.82–1.81), ethyl alcohol (1.84–1.83), dextrose, levulose (1.86–1.87), mannite, dulcite, glycerine, and chloral hydrate.

(*b*) *In all the other cases the molecular depression* $\frac{\Delta}{m'}$ *changes uniformly with the changes in the concentration of the solution.*

This uniform change is a uniform increase as the strength of the solution increases in the case of the three isomers, cane sugar, milk sugar and maltose.

It is a uniform decrease in the case of *n*-propyl alcohol, *n*-butyl alcohol, amyl alcohol, acetone, acetamide, aniline, and salicine. The change is, however, slight in all these cases except that of aniline where the uniform decrease is from 1.86 in extreme dilution to 1.74 at $m' = 0.20$. This is four-fold greater than that observed in any other compound.

4. It appears further that isomeric compounds have very nearly the same molecular depression not only in extreme dilution but also throughout the whole region of concentration which has been examined. Thus the two isomers dextrose and levulose give nearly the same molecular depression. The pair, mannite and dulcite, have also the same values. The same is the case with the three isomers, cane sugar, maltose and milk sugar. In order to justify this statement rather large experimental errors need to be admitted especially in the case of the three sugars, which have the same value of the molecular depression in extreme dilution but which give the following values at $m' = 0.209$:

Cane sugar,	1.892
Milk sugar,	1.876
Maltose,	1.887

These values correspond to the following freezing-points :

Cane sugar,	$-0°.3784$ C.
Milk sugar,	$-0\ .3952$
Maltose,	$-0\ .3774$

To assert, then, that these three isomers have a common value of the molecular depression carries with it the concession of experimental errors in the observations on the solutions $m = 0.20$ amounting to as much as 0°.003 C. It needs, however to be noticed that this is still less than one per cent. of the total depression and I think that an error of this magnitude is possible in the more concentrated solutions due jointly to possible errors in the preparation of the original solutions, to errors in the calculation of m' from observation of the specific gravity of the solution and to the errors of the actual observations of the freezing-point itself.

A final decision of this point should be reserved until the freezing-points of these sugar solutions at $m = 0.20$ are redetermined, one after the other in the closest succession. This I shall undertake at the earliest opportunity.

GENERAL DISCUSSION OF THE RESULTS.

Let us now seek to interpret these experimental results with the aid of the conception of osmotic pressure.

1. The fact that equimolecular solutions of a large number of non-electrolytes in extreme dilution have the same freezing-point indicates that the osmotic pressures of such equimolecular solutions are equal. Or, in other words, the osmotic pressure of non-electrolytes in *extreme aqueous dilution* depends solely on the number of molecules of the given compound in a given volume of the solvent and not on the nature of these molecules. This fact in regard to the osmotic pressure is strictly analogous to a fact in regard to the behavior of bodies in the form of a perfect gas, and known as Avogadro's hypothesis.

The only exceptions so far observed are found in methyl alcohol, ethyl alcohol and acetamide.

A possible explanation of the exceptional character of these compounds was one object of the present work and such an explanation is suggested on page 238.

In order to perfectly interpret the facts presented in the summary of the experimental results in paragraph 2 on page 231, namely that the values of the molecular depression $\frac{\Delta}{m'}$ for a given non-electrolyte either remain practically constant or else change uniformly with the concentration we need to call to mind the theoretical relation which the van't Hoff theory of solution presents between the osmotic pressure and the depression of freezing-point.

By direct application of the second law of thermodynamics to the process by which ice is separated from a solution in course of freezing, van't Hoff has shown that

$$\triangle = \frac{n}{N} \cdot \frac{Tpv}{L} \qquad (1)$$

where the letters have the following significance :

$\triangle$ = depression of freezing-point,

n = number of gram-molecules of solute,

N = number of gram-molecules of solvent,

u = specific volume of solute, or the volume of the solution which contains 1 gram-molecule of solute,

T = freezing-point of solvent in absolute temperature,

L = heat-equivalent of fusion of 1 gram-molecule of the solvent, and

p = osmotic pressure.

Now if the osmotic pressure obeys the laws of Boyle and Gay Lussac, we should have pv equal to RT, and could write the van't Hoff equation in the form,

$$\triangle = \frac{n}{N} \frac{RT^2}{L}, \quad \text{or} \quad \frac{\triangle}{n} = \frac{RT^2}{NL}. \qquad (2)$$

On the left of this equation we have the quotient of the depression of the freezing-point ($\triangle$), divided by the concentration of the solution expressed in gram-molecules (n) of the solute per (N) gram-molecules of the solvent.

This is the molecular depression. On the right we have constant quantities alone, if we make our solution so as always to contain the same amount of solvent.

The equation then asserts the fact that the molecular depression of equimolecular solutions of undissociated compounds in a given solvent is the same for all such compounds, and further remains constant for all the various concentrations of a given compound.

To test the validity of this conclusion by comparing it with the present experimental results, let us suppose our solutions to be so prepared as to contain 1,000 grams of water. Then the van't Hoff equation becomes,

$$\frac{\Delta}{n}=\frac{RT^2}{\frac{1000}{18}\cdot L},$$

or by remembering that $\frac{L}{18}$ is the heat-equivalent of melting 1 gram of ice and denoting this by λ we may write,

$$\frac{\Delta}{n}=\frac{RT^2}{1000\cdot\lambda}. \tag{3}$$

The concentration (n) of the solution is now expressed in gram-molecules of the solute to *1,000 grams* of the solvent, and the molecular depression is the *constant*, $\frac{RT^2}{1000\cdot\lambda}$, the numerical value of which is fixed when we know the values of R, T and λ.

T is of course equal to 273, and R may be taken as 1.98 (gram-calories). The value of λ is generally taken as 79 (gram-calories). If, however, we assume λ equal to 79.3 instead, the value of the molecular depression $\frac{\Delta}{n}$ as given in the van't Hoff equation is 1.86.

Now $\frac{\Delta}{n}$ as here defined is what we have uniformly expressed throughout the experimental work by $\frac{\Delta}{m'}$. This value of the molecular depression is actually found to be 1.86–1.85 for all the non-electrolytes in extreme dilution except three, and is found to remain constant for all the various concentrations of the non-electrolytes, levulose, dextrose, mannite, dulcite, glycerine and chloral hydrate. *These non-electrolytes, then, confirm the van't Hoff assumption that the osmotic pressure obeys the gas laws of Boyle and Gay Lussac.*

The other non-electrolytes are found not to conform to these simple gas laws. Thus the three sugars, cane sugar, milk sugar and maltose exhibit an increase in the value of $\frac{\Delta}{m'}$, with increase in the concentration. From equation (1) then we should conclude that this may be due to the fact that the product (pv) increases with increase of concentration, or these bodies in aqueous solution do not obey Boyle's simple law. The small departure from this law may be perhaps accounted for by use of the same considerations which lead to the application of van der Waals' correction to the volume of a gas when much compressed. The admissibility of such a correction is the more evident if we bear in mind the fact that in the case of these sugars we are dealing with very massive molecules and most likely with unusually large ones as well.

The remaining non-electrolytes all show a uniform decrease of the molecular depression $\frac{\Delta}{m'}$ as the concentration increases. This indicates that the product (pv) of osmotic pressure p and volume v decreases with the concentration. In no case, however, is this decrease more considerable than the decrease in the analogous product in the case of some actual gases, and the departure from the simple law in the present cases may be accounted for by making the obvious assumption that here as in the case of gases an increase in the concentration of the molecules brings about a condition in which the attractions between them begin to play a rôle, the importance of which becomes greater as the solution becomes more and more concentrated. In the case of aniline, however, such an assumption is obviously inadequate to explain the very rapid decrease in the molecular depression, amounting to not less than 7 per cent. between the molecular depression in extreme dilution and that at $m = 0.20$.

The decrease is here so marked that the thought at once suggests itself that it may be due to an "association" of the molecules of this particular non-electrolyte which would decrease the osmotic pressure and so cause a decrease in the value of $\frac{\Delta}{m'}$.

The need of making such an assumption of "molecular association" had not presented itself at any point in the great mass of work already done on the non-electrolytes, and I was unwilling to adopt it in this particular instance until additional experimental material was at hand. For this purpose I entered upon an examination of all available chemical compounds of a constitution similar to that of aniline. There are, of course, only a few such compounds that can be had pure and at the same time sufficiently soluble in water for the present purpose. These are phenol, pyrocatechin, resorcinol, hydroquinone, pyrogallol and benzamide.

Reserving the experimental data for a subsequent paper it may be stated here that each one of these compounds behaves exactly the same as aniline—*the molecular depression decreases at a rapid rate with increase of concentration.* The assumption, then, that the molecules of each of these closely related non-electrolytes combine to form molecular aggregates the number and complexity of which increase with the increase of the concentration is one that easily explains the behavior of this important group of aqueous solutions. We are warranted, I think, in believing that the present facts point to a general law, namely: *The benzene derivatives in aqueous solution exist in the form of molecular aggregates, the number and complexity of which increase with increase in the concentration of the solution.*

The final acceptance of this conclusion can come only after the fullest experimental examination of the matter; and to this end it is important to determine by experiment whether the molecular elevation of the boiling-points and the vapor densities of this group of compounds indicates the same tendency of these compounds to former molecular aggregates. If this should turn out to be the fact there would remain little doubt in regard to the validity of the assumption which is here made in regard to the "association" of these molecules.

In this place attention may be given to the facts presented by the three non-electrolytes, methyl- and ethyl-alcohol, and acetamide. These three compounds exhibit an abnormally low value of the molecular depression throughout the whole range of concentration, and also a slight decrease in the value as the concentration increases.

This latter fact may be easily enough accounted for by the hypothesis that the crowding together of the molecules in the more concentrated solutions brings into play molecular forces which cause the product (pv) to decrease. But how shall we account for the "abnormally" low values which the molecular depressions of these three compounds develop in *extreme dilution.* I am disposed to think that the real explanation lies in the fact which has been brought to light in the case of aniline and its related compounds. Here, as in these other cases, the formation of molecular aggregates may offer a complete explanation.

The very general fact in regard to the increase of the values of the molecular depression $\left(\frac{\Delta}{m}\right)$ as stated in §2 on p. 231 is a mere consequence of the way in which the solutions were prepared, namely so as to contain m gram-molecules per 1,000 cc. of the solution. It is obvious for a given solution containing a given number of grams of the solute and having an observed depression (Δ), that the value of m is less than that of m', and that the difference becomes more and more marked as the strength of the solution increases. This accounts for the fact that the values of the molecular depression $\frac{\Delta}{m}$ diverge upward from that of $\frac{\Delta}{m'}$ with increase of concentration.

3. The results of the experimental examination of the twenty-six various non-electrolytes presented in the present papers and the former one on the same subject shows that none of these compounds exhibit "abnormally high" values of the molecular depression in the region of extreme dilution. In all cases the molecular depression in extreme dilution is either 1.86–1.85 or else it is less than this amount. We thus have at hand a large mass of evidence which shows that *the non-electrolytes do not suffer the slightest dissociation in extreme dilution.*

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THE FORMULA FOR THE DEPRESSION OF THE FREEZING TEMPERATURE OF SOLUTIONS.

BY WILLIAM FRANCIS MAGIE.

THE formula first developed by van't Hoff for the depression of the freezing temperature of a solution below that of the solvent, and commonly used in comparing the results of experiment with the theory, is evidently only an approximate one. In view of the increasing accuracy with which this depression has been measured by Loomis, and the general confirmation of van't Hoff's law which his results furnish, it becomes a matter of interest to inquire whether the departures from the law exhibited by some of his results are due to the insufficiency of the formula or are to be ascribed to other causes. To carry out this inquiry we may use the thermodynamic method introduced by van't Hoff, and proceed to a closer approximation by noticing the circumstances:

1. That the cyclic process employed is not a simple or Carnot's cycle; 2. That many of the quantities which enter the formulas are variable with the temperature.

The solution employed is made up by dissolving n gram-molecules of solute in N gram-molecules of solvent, both n and N being very large numbers. This solution is enclosed in a vessel furnished with a semi-permeable membrane and the following cyclic process is executed with it:

1. The solution being at the absolute temperature t, the freezing temperature of the solvent, a mass of the solvent w is expressed through the membrane. Work will be done by the pressure p required to force out the solvent. On the condition that the quantity of the solution is very great, the pressure will remain constant during this operation and the work done by it in reducing the volume of the solution by the volume v may be represented by pv to any required degree of approximation. At the same time heat will be

developed in the solution, which must be abstracted from the solution to keep its temperature constant. This may be expressed by μv, if μ represents the heat which must be removed in this manner when the volume of the solution diminishes by unity at the temperature t. We may call μ the latent heat of expansion.

2. Heat is then removed from the system at the temperature t, until the expressed solvent is solidified. If we represent by λ the latent heat of liquefaction of the solvent at the temperature t, the quantity of heat thus abstracted is $w\lambda$.

3. The temperature of the system is then lowered by the further abstraction of heat until its temperature becomes t'', the freezing temperature of the more concentrated solution. The heat removed may be represented by

$$s''(W-w)\,(t-t'')+\sigma w\,(t-t'')$$

if s'' and σ represent the specific heats of the more concentrated solution and of the solid solvent respectively and W the mass of the original solution.

4. The solid solvent is then immersed in the solution and melted by the introduction of heat. As it melts the solution will become more dilute and the temperature will rise, until when the melting is completed it reaches the temperature t', the freezing temperature of the original solution. The quantities of heat actually introduced to effect this change might be represented by symbols, and introduced explicitly in the final equations; but it is more convenient to proceed in another way. It has been assumed that the quantity of solvent employed is very great, so that the change in concentration caused by the melting of the solid solvent in it, and so also the rise of the freezing temperature, will be very small. We may therefore set $t''=t'$ and consider the latent heat of liquefaction as constant, to any desired degree of approximation. The heat introduced to melt the solid solvent will then be expressed by $w\lambda'$, where λ' is the latent heat of liquefaction at the temperature t'. The heat introduced to raise the temperature of the solution from t'' to t' will be balanced in the final equations by that abstracted in lowering the temperature of the solid solvent and of the solution from t' to t'' in operation 3 to a degree of approximation which may be made

as close as we please by the use of a very great amount of solution.

5. The solution is then raised to its original temperature t by the introduction of the quantity of heat represented by $s'W(t-t')$, if s' represents the specific heat of the original solution.

The cyclic process is then complete. It is a reversible process and we may accordingly write the equations of energy and entropy for it. Considering $t''=t'$, these become

$$(a) \quad \mu v + w(\lambda - \lambda') + \{s''(W - w) - s'W + \sigma w\}(t - t') = pv.$$

$$(b) \quad \frac{\mu v}{t} + w\left(\frac{\lambda}{t} - \frac{\lambda'}{t'}\right) + \{s''(W - w) - s'W + \sigma w\}\int_{t'}^{t}\frac{dt}{t} = 0.$$

The integral $\int_{t'}^{t}\frac{dt}{t} = \log\frac{t}{t'}$ which occurs in equation b may be expanded in a series of which it will be sufficient to retain the two terms, $\frac{t-t'}{t'} - \frac{(t-t')^2}{2t'^2}$. Dividing equation a by t', combining the two equations and reducing, we obtain

$$(c) \quad (t-t')\left\{\mu v + w\lambda + [s''(W-w) - s'W + \sigma w]\frac{t-t'}{2}\cdot\frac{t}{t'}\right\} = tpv.$$

This equation is valid for any solution, whatever the solute may be, and however much dissociation or association there may be in the solution. It involves only the assumption that a definite pressure exists by which the solvent may be forced out of the solution through a semi-permeable membrane. The approximations involved in it, except that in which the third and subsequent terms of the expansion of $\log\frac{t}{t'}$ are neglected, depend on the amount of the solution employed, and may be pushed to any degree required by the use of a sufficiently large amount of the solution.

The term in the parenthesis which is of the most importance is $\omega\lambda$. Neglecting the other terms in the first approximation we obtain van't Hoff's formula for the depression of the freezing temperature

$$(d) \qquad t - t' = \frac{tpv}{w\lambda}.$$

We may substitute this value of $t-t'$ in the specific heat term in the parenthesis, setting $\frac{t}{t'} = 1$, and obtain a formula for the depression of the freezing temperature which is correct to a second approximation.

In case the solution is one in which the osmotic pressure is proportional to the absolute temperature I have shown in a previous paper[1] that

$$(e) \qquad \mu = p$$

and that

$$(f) \qquad s''(W - w) - s'W + sw = 0,$$

where s represents the specific heat of the solvent.

In that paper it was shown by experiment that the relation embodied in equation f holds true for many solutions of non-electrolytes in water. For these solutions equation e will also hold true.

The general formula may therefore be modified for the case of non-electrolytic solutions into the form

$$(g) \qquad (t - t')\left\{w\lambda + pv + [\sigma - s]\frac{tpv}{2\lambda}\right\} = tpv.$$

If we set M for the mass of the solvent and n for the number of gram-molecules of solute dissolved in it, and assume that the mass w is the mass of solvent which is associated with one gram-molecule of solute in the solution, we obtain for the molecular depression in terms of a standard M,

$$(h) \qquad \frac{t - t'}{n} = \frac{tpv}{M\lambda + npv + (\sigma - s)\frac{ntpv}{2\lambda}}.$$

The volume v is the volume which contains one gram-molecule of solute in the solution.

This formula holds whether or not the osmotic pressure conforms to Boyle's law but requires a constant ratio between the osmotic pressure and the absolute temperature. If the osmotic pressure conforms to the laws, of gases, we may write $pv = Rt$, where R is the gas-constant, and may calculate the depression and examine the influence of the correction terms of the denominator upon its value. Setting $R = 84490$, in which the gram-weight is the unit of force, λ for water $= 79.3$[1] and $M = 1{,}000$ grams we obtain in the first approximation $\frac{t - t'}{n} = 1.855$. Further, setting $\sigma = 0.5$ calorie and $n = 1$, we find that the effect of the two correction terms, which are nearly equal and of opposite sign, is to reduce this value only by 0.001 or to 1.854; an effect far too small to be detected by the present methods of measurement. These terms will be of similar magnitude relative to the principal term of the denominator in any solution that is fairly dilute. It appears, therefore, that the first approximation gives us a formula which is sufficiently exact for our present needs and that the departures exhibited by many solutions from the law of proportionality between the depression of the freezing temperature and the concentration are to be accounted for on other grounds than the insufficiency of the ordinary formula.

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[1] PHYSICAL REVIEW, Vol. IX., No. 2, August, 1899.

Princeton University.

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[1] Loomis, Physical Review, Vol. IX., No. 5, November–December, 1899.

ON THE ACTION OF THE COHERER.

By K. E. Guthe.

I. The Critical Voltage.

In a former paper[1] Trowbridge and I have shown that a coherer with one contact shows quite a regular behavior, when cohesion is produced by a current flowing through it. Its P. D. during the passage of the current increases with the latter, finally reaching a constant value which is independent of a further increase of the current, or changes in the applied E.M.F. We have called this value the critical voltage of the coherer and have determined the same for a few metals.

It has seemed of interest to extend the investigation to a larger number of metals, and the present paper contains the results with coherers of silver, copper, zink, aluminium, cadmium, tin, iron, German silver, nickel and bismuth.

The coherer had practically the same form as the one described in the former paper. Instead of metal balls I used spherical surfaces stamped out of metal sheet. The coherer had one contact only and its resistance could be adjusted by means of a fine screw.

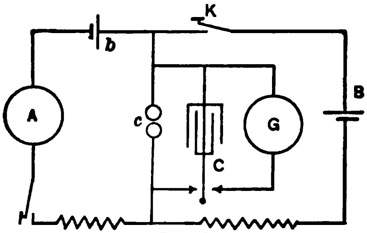

Fig. 1.

The method employed is illustrated by Fig. 1; in which c is the coherer. In order to estimate its original resistance it was connected with an auxiliary circuit containing a low E.M.F. ($b = 0.4$ V.) and a milliammeter (A). After adjustment to a high resistance, cohesion was produced by closing the key K; while the current was flowing, the condenser C was charged and discharged though the galvanometer (G) which had been previously calibrated by means of a standard cell. Thus the P. D. at the terminals of the coherer could easily be calculated from the deflection of the galvanometer. After opening the key K, the auxiliary circuit was closed again, to ascertain if a lowering of resistance had taken place. Since it was desired to determine the critical voltage only, no accurate measurements of the current were made, though I assured myself in every case by varying the current, that the critical voltage had been reached.

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[1] Guthe and Trowbridge, Phys. Rev., XI., p. 22, 1900.

(*a*) *Contact Between Surfaces of the Same Metal.*

For each metal I took a series of 30 to 40 observations. The deflections due to the discharge of the condenser varied very little in each series. In the following table the mean values of the deflections (d) and the critical voltages (V) are given.

Table I.

	Ag.	Cu.	Zn.	Al.	Cd.	Sn.	Fe.	Germ. S.	Ni.	Bi.
d	13.7	21.6	22.2	54.3	25.1	21.9	51	32	46.9	42
V	0.062	0.094	0.096	0.236	0.109	0.095	0.222	0.139	0.204	0.183

It will be seen that the critical voltage varies appreciably where different metals are used; for German silver it lies between those of its constituent parts. The critical voltage seems to stand in a certain relation to the atomic weight of the metal. If we multiply the two together, we obtain the following results:—

Table II.

Ag.	Cu.	Zn.	Al.	Cd.	Sn.	Fe.	Ni.	Bi.
6.71	5.96	6.18	6.39	12.22	11.22	12.43	11.93	39.06

Ag, Cu, Zn and Al give practically the same product: 6.31; Cd, Sn, Fe, Ni, a value almost twice as large: 11.95, while Bi stands alone with a product six times larger than the smallest: $39.06 = 6 \times 6.51$. In the paper mentioned above we found for Pb, $V = 0.127$ volt which gives, multiplied by the atomic weight of Pb; $26.28 = 4 \times 6.57$. The first four metals are the best conductors of heat or electricity, while Pb and Bi stand alone in this respect also.

Interesting as this distinct division of the metals into three groups is, especially when we consider the great differences in the atomic weights of metals in the same group, there is not enough material on hand to form any definite hypothesis as to the reason for it.

(*b*) *Contact Between Surfaces of Different Metals.*

In the former paper a close agreement was noted between the formula expressing the P. D. of the coherer as a function of the current and the formula[1] which I have found to represent the polarization of Cu electrodes in $CuSO_4$ solution, and we were led to believe that we had to do with a phenomenon somewhat similar to the electrolytic conduction of electricity. We assumed that the existence of a critical voltage is due to the resistance of a layer of small metallic particles (ions or electrons) carried over by the current.[2] Supposing that these particles travel in the direction of the current, we might expect when working with a coherer, having different metals at the two sides of the contact, to obtain the critical voltage of the one or the other metal according to the direction of the current. That this is not the case is shown by the data in Table III. in which are given the critical voltages for a large number of combinations. The current is supposed to flow from the metal in the horizontal to that in the vertical line. The method of observation was the same as in the preceding experiments.

TABLE III.

From :

To:	Ag.	Cu.	Zn.	Cd.	Sn.	Fe.	Germ. S.	Ni.	Bi.
Ag.	0.0622	0.082	0.125	0.127	0.164	0.156	0.078	0.209	0.13
Cu.	0.086	0.094	0.135	0.142	0.170	0.252			0.13
Zn.	0.119	0.143	0.096	0.109	0.103	0.141			0.117
Cd.	0.118	0.131	0.105	0.109	0.087	0.174	0.091		
Sn.	0.166	0.179	0.089	0.087	0.095	0.210	*c* 0.2	0.152	*c* 0.13
Fe.	0.300	0.278	0.141	0.152	0.152	0.222	0.243	0.300	0.22
Germ. S.	0.078			0.10	*c* 0.20	0.261	0.139	0.170	0.165
Ni.	0.122				0.109	0.287	0.191	0.204	0.117
Bi.	0.26	0.261	0.196		*c* 0.22	0.304	0.209	0.196	0.183

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[1] Guthe, PHYS. REV., VII., p. 193, 1898.

[2] It can easily be shown by a measurement of the resistance of the coherer, by means of an alternating current, that we have a *metallic* contact, after cohesion has taken place. Using the well-known Kohlrausch method for measuring electrolytic resistances, the value found agreed well with the one calculated from the P. D. and the current. The telephone could be adjusted to absolute silence which shows conlusively the existence of an actual metallic contact.

The deflections of the galvanometer were in general quite concordant; only with Al as one side of the coherer the results were so unsatisfactory that they have been omitted from the table.

We see that in general the direction of the current has no appreciable influence upon the critical voltage between different metals. Differences of considerable size were observed between Bi and Ni and between Fe and Sn only. The Peltier effect can hardly be adduced as the sole explanation for these differences, since they are in opposite direction for Bi and Ni and do not appear for German silver at all. We shall see under III. that the heating of the point of contact may have an influence upon the critical voltage and may possibly explain the observed differences due to the direction of the current.

II. THE NEGATIVE ACTION OF THE COHERER.

Under "negative action" I understand the increase of resistance which can sometimes be observed in coherers when responding to an electrical influence. All the metals studied by me, especially the soft metals, show this behavior under certain conditions. Bose[1] has recently declared this negative action to be the normal one for certain metals. He supposes that each metal exists in two modifications, one with a high resistance (modification *A*) and another with a low resistance (modification *B*). The difference between these two, he thinks, is to be sought in the different arrangement of the molecules in the two cases. In certain metals, which he calls positive, *e. g.*, Fe, the modification *A* is the normal, in others, *e. g.*, K modification *B*. Under the influence of an electric wave the surface of the metal is supposed to change from its normal state into the other, and thus strains are produced in the metal. Though further action of the electric waves the new arrangement of the molecules may suddenly break down and the resistance of the coherer return more or less to its original value. Thus "oscillatory changes in the molecular structure are produced, which are evidenced by the corresponding electrical reversals."

Bose used in all his experiments the ordinary form of coherer, having a great number of contacts. Mizuno[2] investigating the influence of repeated electrical impulses upon the resistance of such coherers, found curves of very similar character to Bose's for positive metals; even potassium showed a large final drop in resistance instead of an increase which should have been expected according to Bose's theory. In one case Mizuno used a one-contact coherer (two lead balls) and here the resistance fell after a few sparks of the oscillator to a constant minimum without showing any reversals at all.

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[1] Bose, Proc. Roy. Soc., 65, p. 166, 1899 and 66, p. 450, 1900.

[2] Mizuno, Phil. Mag., 50, p. 445, 1900.

It seems possible to arrive at an explanation of the negative action only from experiments with a coherer of a similar form. The phenomenon as observed by me, was as follows: On the first adjustment of the coherer the needle of the milliammeter showed quite irregular movements before it became steady. On closing the main circuit the resistance increased, but when, by opening key K the auxiliary circuit was closed, I observed an unsteady, slowly increasing deflection of the milliammeter showing that the low resistance was formed again. This corresponds perfectly to Bose's description "of the rumbling noise in the telephone due to the rearrangement of the surface molecules to a more stable condition."

It suggested itself immediately that a small, loose particle formed a conducting bridge between the coherer surfaces, which was thrown aside on the introduction of a higher E.M.F., but fell back to its original position, when only a low E.M.F. was in the circuit. This would be quite similar to the action of Nengschwender's anticoherer. The following observations showed this supposition to be true.

While under normal conditions a slight increase of pressure reduced the resistance almost to zero, it remained always relatively high in spite of an appreciable pressure, when the coherer showed negative action. The conducting particle remained between the surfaces.

The increase of resistance could be brought about many times in succession, if the coherer was left undisturbed. Sometimes the resistance became infinite and remained so. In such a case the surfaces had to be brought nearer together in order to make a new adjustment to a high resistance possible. After this the normal action took place. The particle had been thrown aside.

This shows that the negative action of the coherer is due to disturbing influences and cannot be considered a normal phenomenon, as Bose supposes. We shall not be able to understand the nature of the coherer unless we experiment with coherers of a form as simple as possible. The usual form, it seems, is not at all suited to the purpose.

In a paper, which has just appeared, Marx[1] describes his experiments with the so-called Schaefer anticoherer. The original resistance of this instrument is due to small particles forming a bridge between the two metallic ends. He observed under the microscope a distinct motion of the particles when an electric wave fell upon the apparatus, and a falling back into their original position when the electrical influence ceased.

III. The Influence which the Heating of the Contact has upon the Resistance of the Coherer.

It is well known that, after cohesion has taken place, a slight heating of the coherer restores the original high resistance; but it would be wrong to conclude from this that a coherer is less sensitive at higher temperatures. Considering the smallness of the contact, there can be no doubt that even with small currents a development of heat must take place at that point. With metals of low melting point I had observed the heating effect during the previous experiments. In general I was unable, when examining the contact by means of a microscope, before and after being used, to detect the slightest change on the metallic surfaces. But in the case of Bi and Sn, melting took place when the current was increased to more than one ampère. With the other metals I could not observe any change even with currents as large as four ampères.

In the course of my experiments on this subject I was led to the observation of a phenomenon, which, as I believe, was hitherto unknown. The method was practically the same as above. The coherer was slightly changed by using two fine wires of the same metal and at right angles to each other instead of the spherical surfaces. By a light pressure against one of them the loose contact was effected. Now I sent by means of a separate circuit a current of such strength through one of the wires that it—and consequently the point of contact too—became heated. While the heating took place the main circuit was closed and the P .D. of the coherer measured.

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[1] Marx, Phys. Zeitschr., Jan. 26th, 1901.

The higher the temperature of the contact, the lower appeared the resistance of the coherer under otherwise similar conditions and the resistance returned to its original high value when the heating ceased.

The following tables may serve to illustrate this phenomenon. In the first column I have given the deflections obtained by the discharge of the condenser when cohesion was produced before the contact was heated. In the second column follow the deflections obtained while the heating took place, and columns 3 to 5 give the corresponding deflections 10, 20 and 50 seconds after the heating had ceased. The coherer consisted of steel wires of 0.36 mm. diameter. Unit deflection corresponds to 0.00435 volt.

Table IV.

174	3	31	102	160
121	23	56	159	160

Even when the original resistance was infinite (this may be expressed by ∞) the phenomenon could be very distinctly observed.

Table V.

∞	18	292	∞	∞
∞	19	229	∞	∞

The results obtained when the current through the wire and consequently the temperature of the contact was varied, are given in Table VI. In the first column the heating current is given, the following columns have the same meaning as before. The values in the second column depend on the accidental original adjustment.

Table VI.

0.2 amp.	138	121	122	139	139
0.5 amp.	90	12	95	95	95
4.0 amp.	86	5	11	34	75

Similar results were obtained with copper wires. With them the heating seemed to have a still larger influence than with steel. The deflections were only two or three scale divisions during the heating, even in cases in which the original resistance had been infinite. The lengthening of the wire due to the higher temperature produced slipping and made the observations rather difficult, but this could easily be avoided by holding the wire in its original horizontal position with a fine vertical spiral.

Finally I used a contact between wires of different diameter. If we produce cohesion in such an instrument by sending a relatively large current through both wires, the thinner wire will be heated. The observations showed now a decided influence of the direction of the current. This can hardly be due to the different curvature of the wires, since Trowbridge and I have shown, at least for steel balls, that the diameter has no influence upon the critical voltage.

I select for illustration one example out of a great many. The thickness of the steel wires was 1.65 and 0.27 mm. respectively. When a current of three ampères was sent from the thicker to the thinner wire I obtained by discharging the condenser a deflection of 136 scale-divisions. If the current is smaller, the differences are smaller. The P. D. of the coherer is therefore lower if the electricity flows from the hotter to the colder side than if it flows in the opposite direction.

This may enable us to understand why different critical voltages were obtained according to the direction of the current, when contacts with different metals were used (Table III.). Bi showed the discrepancy most of all. If Bi forms one side of the coherer this side will be much warmer than the other, since this metal is a very bad conductor of heat. This would demand a small P. D. if the current flows from Bi to another metal. On the other hand when a current flows in this direction the point of contact is cooled and we might expect a higher critical voltage. These two influences are doubtless of a secondary nature and must be superposed. With Bi, as Table III. shows, the influence of the difference in temperature is by far the greater, while with Ni the Peltier effect seems to be the stronger.

I believe that in the action of the coherer the heating of the contact plays an important rôle. By it the first impulse to the lowering of resistance is given ; it may be called the first stage. We have to keep in mind that when the contact is not heated by the current passing *through* the coherer, the resistance very soon increases on cooling, while after actual cohesion has taken place, a metallic contact is produced and the resistance returns only very slowly to its high value.

PHYSICAL LABORATORY, UNIVERSITY OF BERLIN, January, 1901.

NEW BOOK.

Livre Jubilaire: Recueil travaux offerts par les auteurs à H. A. LORENTZ, professeur de physique à l'université de Leiden. Le Haye; Martinus Nijhoff, 1900. Pp. ix + 678.

The eleventh of December, 1900, was the twenty-fifth anniversary of the conferring of the doctor's degree upon the eminent physicist, H. A. Lorentz; and the occasion was celebrated by the presentation to him on behalf of his colleagues of a very notable collection of memoirs gathered together in a jubilee volume. The committee consisting of Professors Booscha, Haga, V. A. Julius, W. H. Julius, Onnes, Siertsema, Sissingh, VanderWaals, Wind and Zeeman are to be congratulated upon the brilliant success of their work. The collection is the more remarkable when we consider the short time allowed to the various authors for the completion of their work. It consists of 58 papers which make a book of nearly seven hundred pages. These were published as a separate volume of the Archives of the Society of Sciences at Harlem.

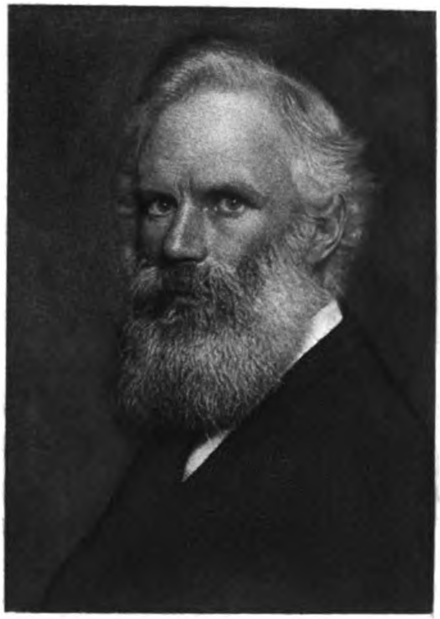
Of the purely theoretical papers which constitute the most important part of the collection, eighteen deal more or less directly with problems arising from the consideration of the mechanics of the ion, the foundation of the theory of which is largely due to Lorentz. To this group belong the contributions of V. A. Julius, Farkas, Wien, Kaufmann, Planck, Riecke, Poincaré, Righi, Voigt, Sagnac, Cohn, Garbasso, Wiechert, Wind, J. J. Thomson and des Coudres. Boltzmann in a brief note and Berthlelot at considerable length discuss the equation for the pressure of gases and in particular the expression of the same deduced by Lorentz.

There could scarcely be imagined a more gratifying tribute to the genius of that physicist nor better illustration of the deep impression made upon the mathematical physicists of our day by the views propounded by him in the famous memoir entitled, *Versuch einer Theorie der Elektrischen und optischen Erscheinungen in bewegten Körper* (Leiden, 1895). The development of the theory at the hands of the writers just named leads to a number of startling conclusions. We are told that gravitational disturbances are transmitted with velocity equal to that of light; that gravitation itself is modified by the motion of the attracting bodies; that mass as defined in terms of inertia is constant only for small velocities and increases with the velocity of the moving body; that the first and second of Newton's Laws of motion are to be regarded as rigorous only when we take into account the effects of motion in the surrounding ether; that the principle of equality of action and reaction is not rigorously applicable when applied to matter alone. The modifications which the establishment of these new views would compel us to introduce into the older mechanics become appreciable only when we have to deal with very high velocities. It is chiefly by the careful study of planetary motion or possibly in the domain of the kathode rays that we may, if at all, look for experimental verification of the theory. Poincaré at the close of his paper cites a computation by Lienard to the effect that the complementary force necessary to balance the recoil of a machine of 100 kilowatts would be only $\frac{1}{600}$ of a dyne.

That the Lorentz Jubilee volume, in addition to these papers which deal more or less directly with theoretical issues raised by him, contains much other interesting material will be seen from the following table of contents:

Bernard Brunhes, Sur la réflexion interne dans un cristal doué du pouvoir rotatoire; V. A. Julius, Sur l'action subie par un conducteur chargé dans un champ d'intensité constante; Lord Rayleigh, On the stresses in solid bodies due to unequal heating, and on the double refraction resulting therefrom; H. Pellat, Réflexions au sujet de l'univers et des lois naturelles; Wilder D. Bancroft, Reaction velocity and solubility; Edm. van Aubel, Sur les résistances électriques des métaux purs; Julius Farkas, Allgemeine Principien für die Mechanik des Aethers; Ludwig Boltzmann, Notiz über die Formel für den Druck der Gase; E. Mathias, Sur la loi de distribution de la composante horizontale du magnétisme terrestre en France; W. Wien, Ueber die Möglichkeit einer elektromagnetischen Begründung der Mechanik; G. Tammann, Ueber die Lage der Volumen- und Energiefläche eines Krystalls und seiner Schmelze; N. Schiller, Einige thermodynamisch abzuleitenden Beziehungen zwischen den Grössen, die den physikalischen Zustand einer Lösung characterisiren; W. Kaufmann, Ueber die Schwingungsamplitude der Electronen; A. Turpain, Etude expérimentale sur le résonnateur de Hertz; Max Planck, Ueber die von einem elliptisch schwingenden Ion emittirte und absorbirte Energie; G. Guglielmo, description d'une simple balance magnétique; Eduard Riecke, Ueber characteristische Curven bei der electrischen Entladung durch verdünnte Gase; G. J. W. Bremer, Indices de réfraction de solutions de chlorure de calcium; F. A. H. Schreinemakers, La tension de vapeur de mélanges ternaires; P. Duhem, Sur la théorie électrodynamique de Helmholtz et la théorie électromagnétique de la lumière; P. Zeeman, Weiteres zur unsymmetrischen Aenderung der Spectrallinien in einem Magnetfelde; H. du Bois, Toupie magnétocinétique; illustrant les phénomènes para- et diamagnétiques; H. Poincairé, La théorie de Lorentz et le principe de la réaction; G. H. Bryan, Energy accelerations. A study in energy partition and irreversibility; Ernest Cohen, Ueber die Bestimmung der Arbeit, welche die Verwantschaft leisten kann; J. P. Kuenen, Mixtures of hydrochloric acid and methylen ether; G. Bakker, Théorie de l'induction

électrique ; A. Cornu, Deux méthodes optiques pour l'étude de l'élasticité des corps solides ; E. L. Nichols, On a new method of calibrating thermo-electric elements for use in the measurement of high temperatures ; Auguste Righi, Sur les ondes électromagnétiques d'un ion vibrant ; William Ramsay, Notes on the refractivities of the inactive gases ; H. W. Bakhuis Roozeboom, Sur l'équilibre de cristaux mixtes avec la phase vapeur ; W. Voigt, Ueber das electrische Analogon des Zeeman-Effectes ; G. Sagnac, Relations nouvelles entre la réflexion et la réfraction vitreuses de la lumière ; J. Pernet, Ueber einen Drehkomparator zur Vergleichung und Ausdehnungsbestimmung von Massstäben ; J. D. van der Waals, Sur la relation entre les modifications, subies par le volume spécifique de la vapeur saturée et celui du liquide coexistant sous l'influence des variations de température ; Daniel Berthelot, Quelques remarques sur l'équation caractéristique des fluides ; L. H. Siertsema, Die Dispersion der magnetischen Drehung der Polarisationsebene in negativ drehenden Salzlösungen. Messungen mit rothem Blutlaugensalz ; P. van Everdingen, Jr., Ueber eine Erklärung der Widerstandszunahme im Magnetfelde und verwandter Erscheinungen in Wismuth ; D. A. Goldhammer, Ueber den Druck der Lichtstrahlen ; J. J. van Laar, Ueber die Ableitungen des thermodynamischen Potentials nach T und p bei zusammengesetzten Komponenten ; W. H. Julius, Bemerkungen über einige Grundsätze der Elektricitätslehre ; N. Kasterin, Ueber die Ausbreitung der Wellen in einem nicht homogenen Medium von lamellarer Structur ; Emil Cohn, Ueber die Gleichungen der Electrodynamik für bewegte Körper ; A. Garbasso, Ueber eine Darstellung der lichtdrehenden Körper ; J. Bosscha, Remarques sur les normales barométriques et leur usage dans la prévision du temps ; H. G. van de Sande Bakhuyzen, Quelques remarques sur la réduction des positions des étoiles mesurées sur les clichés photographiques ; E. Wiechert, Elektrodynamische Elementargesetze ; Max Reinganum, Ueber die molekulare Ahziehung in schwach comprimierten Gasen ; H. Haga, Ueber den Versuch von Klinkerfues ; J. D. van der Waals, Jr., La propagation libre de la radiation est-elle réversible ? ; Ernst Dorn, Versuche über Secundärstrahlen ; C. H. Wind, Ueber das Feld langsam bewegter Electronen ; Ch. M. A. Hartman, Beiträge zur Kenntnis der Van der Waals'schen ψ-Fläche. III. Die Condensations-Erscheinungen bei Mischungen von Chlormethyl und Kohlensäure für 9°,5 ; J. J. Thomson, On a view of the constitution of a luminous gas, suggested by Lorentz's theory of dispersion ; J. E. Verschaffelt, Contributions à la connaissance de la surface ψ de Van der Waals. La loi des états correspondants, dans les mélanges d'anhydride carbonique et d'hydrogène ; Th. des Coudres, Zur Theorie des Kraftfeldes electrischer Ladungen, die sich mit Ueberlichtgeschwindigkeit bewegen ; H. Kamerlingh Onnes, Die reducirten Gibbs'schen Flächen.



GEORGE FRANCIS FITZGERALD

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PHYSICAL REVIEW.

SURFACE TENSION AT THE INTERFACE OF TWO LIQUIDS DETERMINED EXPERIMENTALLY BY THE METHOD OF RIPPLE WAVES.

BY FLOYD R. WATSON.

THE method of ripple waves used in determining surface tensions of liquids is well known. Thomson[1] advanced the theory that, when the length of waves on the surface of a liquid is small, the vibration of the waves depends chiefly upon capillarity. The formula deduced in accordance with this theory is as follows,

$$T = \frac{n^2\lambda^3}{2\pi}(\rho_1 + \rho_2) - \frac{g\lambda^2}{4\pi^2}(\rho_1 - \rho_2)$$

where T is the surface tension, λ the wave-length, n the frequency of the waves, g the acceleration of gravity, ρ_1 the density of the lower liquid and ρ_2 the density of the upper. In case the upper liquid be air, ρ_2 may be neglected, and the formula becomes

$$T = \rho_1\left(\frac{n^2\lambda^3}{2\pi} - \frac{g\lambda^2}{4\pi^2}\right).$$

Lord Rayleigh[2] was the first to use this theory to determine surface tension, his general method being to excite the surface of water periodically and view, by means of interrupted light, the waves formed; the flashes of light being isoperiodic with the waves —the so-called stroboscopic method. Later Dorsey,[3] Smith,[4] Barnett[1] and others used Rayleigh's method with more perfected apparatus.

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[1] Phil. Mag., (4), 42, 375.

[2] Phil. Mag., (5), 30, 386.

[3] PHYS. REVIEW, 5, 170, 213.

[4] Proc. Roy. Soc. Edinb., 17, 115.

During two years, 1898–1900, while at the University of California, the author devoted some time to the study of surface tension. The first part of the work was a verification of Lord Rayleigh's experiment, his method being used and his apparatus duplicated as far as possible. Later both the method and the apparatus were improved until consistent results were obtained. Further work on the same problem has been done by the author at Cornell University, where still better methods were used with more refined apparatus.

By means of measurements taken, surface tensions were calculated for mercury, water, petroleum, benzine and alcohol when these liquids were in contact with air. By a modification in the apparatus, measurements were taken giving interfacial tensions for mercury-water, mercury-alcohol, water-petroleum and water-benzole. The method was perfected for measuring surface tension between any two liquids that do not mix or unite chemically.

Description of Apparatus.

The apparatus and method used at the University of California will be described first and a table of results given. Later the work at Cornell will be described and comparisons made.

Figure 1 gives a diagrammatic sketch of the apparatus used in generating the waves and measuring their length. The waves were generated on the liquid in the pan *A* by means of the glass microscope slide *D* attached to the end of the tuning fork prong *B*. Fork *B* is attached to fork *C* by a wire *E*, the ends of the wire being fastened securely to the prongs of the forks as shown in the figure. Fork *C* is run electro-magnetically, the amplitude of vibration of its ends being about ¾ cm. Fork *B* is vibrated by the mechanical impulses sent along the wire *E*, both forks thus vibrating in unison. At first fork *B* was run by a shunted circuit from fork *C*, but the vibrations of the forks were then not always in unison, nor were their movements steady. An attempt was made

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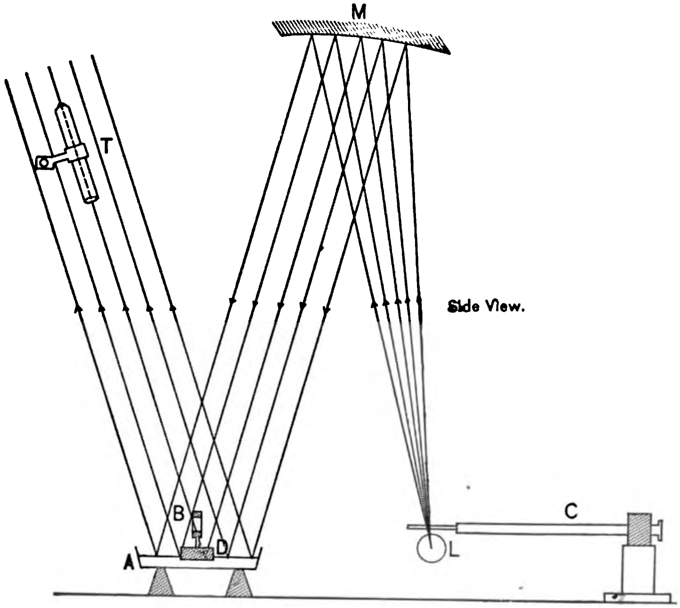
[1] Phys. Review, 6, 257.



Side View.

Top View.

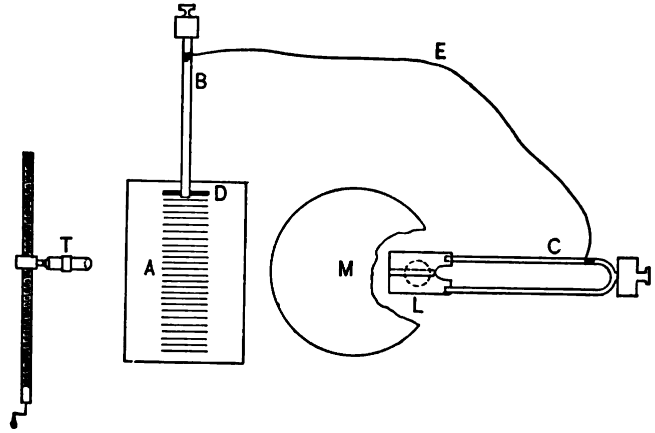


Fig. 1.

Sketch of apparatus.

to vibrate fork *B* without shunting the current from *C*. This was done by placing the fork *B* so that its prongs were in the same plane with those of *C* and connecting adjacent prongs with a taut string, fork *C* being run electro-magnetically as before. This method worked well even after the string became somewhat loose. The last fact suggested to the author the plan of connecting the forks with a wire, so that they could be placed more conveniently for the purposes of the experiment. The plan was found to be successful—the forks vibrating steadily and in unison when separated by a distance so great as 6 feet. Later at Cornell, the author replaced fork *B* by a stick of wood, which vibrated equally as well as the fork.

The light was given by a 50 candle-power incandescent lamp whose filament was wound in the shape of a hollow cone, giving an intense concentrated source of illumination. The light was interrupted by the fork *C*, passed to the concave mirror *M*, and was rendered parallel by reflection, after which it was reflected from the surface of the liquid to the telescope *T*. The light was made intermittent by means of two small strips of wood attached to the prong ends of the fork *C*. The strips overlapped when the fork was at rest, and let the light through once each vibration when the fork prongs were in their position of extreme outward swing, thus making the flashes of light isoperiodic with the waves generated by fork *B*.

The telescope was moved by an endless screw so that its successive positions were parallel. The concave mirror was of glass, its rear surface being the reflector. Its diameter was about 30 cm. and its focal length 84 cm. The most satisfactory pan for holding the liquid was one of galvanized iron 24 by 27 cm. and 3 cm. deep. To prevent the vibrations carried by the floor from disturbing the surface of the liquid, the pan was set on a small wooden frame which had rubber tubing nailed to its upper surface, and had each of its four supports resting in a box of sand.

When the apparatus was properly arranged for taking measurements, the source of light, the axes of the telescope, mirror and fork *C* should lie in a plane perpendicular to the liquid, and the waves on the surface should be parallel to this plane.

INTERFACIAL WAVES.

Waves at the interface of two liquids such as mercury and water were obtained by having the glass vibrator on the prong of fork *B* immersed just below the mercury-water surface. The waves on the upper surface of the water were found to distort the appearance of waves at the interface, so a thin strip of glass was placed close to the vibrator and parallel to it with its lower edge immersed in the water surface, thus stopping the surface waves and allowing a clear view of the interfacial waves.

In the case of two liquids, such as water and oil, it was found that the reflection of light from the upper surface was so strong as to drown out the view of the waves at the interface. To remedy this trouble a piece of plate glass was suspended nearly parallel to the interfacial surface with its lower side just submerged in the oil. This arrangement caused the light striking the upper surface of oil to be reflected at a different angle from that of the light reflected from the interface, hence the waves could be seen. (See Fig. 2.)

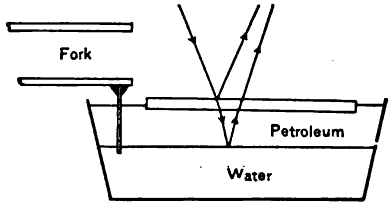


Fig. 2.

METHOD OF TAKING MEASUREMENTS.

Everything that the liquid was to touch was thoroughly cleaned, first with acid, then with alcohol and finally with running tap water. The liquid whose tension was to be determined was poured in the pan to a depth of at least a centimeter, the glass vibrator on the end of the fork was adjusted so that it dipped just below the surface and was perpendicular to it. The vibration of the fork was regulated until the waves were steady. A narrow strip of German plate glass, ruled crosswise at certain known distances, was placed parallel to the surface of the liquid and as close as possible to the waves without touching them. By means of the traveling telescope the number of waves were then counted between the ruled cross lines. Having the ruled glass plate so close to the surface threw out any error due to the light rays not being parallel, or an accidental shifting of the telescope. Usually from 30 to 40 waves were counted and tenths of waves estimated. The readings were verified by running the telescope backwards and taking the readings again in the reverse order. Reflected waves were met with at times, but they were reflected from the end of the pan which was parallel to the glass vibrator, and hence caused no distortion.

To determine *n*, the frequency of the waves, it is only necessary to determine the period of either fork, the periods of the forks and the waves being the same. The method first used was a chronograph method, where the fork's vibrations were traced by the side of a standard time circuit trace. Trouble was encountered in this method, in that the shunt from the interrupting fork *C* caused the fork to run unsteadily and probably change its period slightly. To obviate this difficulty, an auxiliary circuit was established (see Fig. 3). A small light strip of hard rubber, *AB*, was screwed to the fork and at *A* a small wire was threaded through. Each end of this wire dipped into a small mercury cup. As the fork vibrated the wires dipped into the mercury once each vibration closing the auxiliary circuit *ADCEA* which made the fork's trace on the chronograph. The strip of rubber was left on the fork so as not to alter the period.

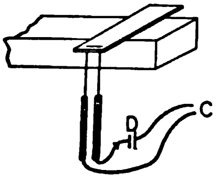


Fig. 3.

Another more convenient method used was to place a standard Koenig fork with a vibration microscope just over the interrupting fork and parallel to it, so that the flashes of light were viewed through the microscope when both forks were in motion. The light appeared to move back and forth, corresponding to beats. The number of these excursions, or beats, in a given time was counted, and knowing the pitch of the standard fork, the frequency of the interrupting fork, and hence that of the waves, was calculated.

The value taken for *g* was 980 cm. per sec. per sec., though the local value at Berkeley was 979.8, the error being small compared with the error in measuring λ. The density for water was taken to be 1, and for mercury 13.6. Temperatures and densities were determined by standard instruments. To reduce the value of the tensions to 0° C. the following formula[1] was used:

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[1] Dorsey, Phil. Mag., Nov., 1898, page 388.

$T_t = T_0 (1 - at)$ where t is the observed temperature, T_0 the tension at 0° C. and $a = .0020$.

In the following table ρ gives the density, t the temperature in degrees Centigrade, λ the wave-length in centimeters, n the vibration frequency of the fork, and T_0 the surface tension in dynes per cm. at 0° C.

Table I.

Date.	Liquid.	ρ	t	λ	n	T_0
Aug. 10	Distilled water	.997	16.6	.5200	58.75	77.93
" 14	" "	"	16.8	.5263	"	76.24
" 15	" "	"	16.6	.5263	59.00	76.21
" 17	" "	"	18.7	.5263	"	76.54
" 17	" "	"	18.7	.5264	"	76.56
" 18	" "	"	16	.5263	"	76.11
" 24	" "	"	19.8	.3300	115.50	76.72
" 13	Mercury	13.6	18.2	.4039	58.75	433.25
" 15	"	"	16.6	.3967	59.00	432.01
" 17	"	"	16	.3994	"	440.18
" 17	"	"	18.7	.3984	"	439.22
" 18	"	"	16	.4000	"	442.25
" 20	"	"	18.1	.3984	"	438.67
" 22	"	"	18.7	.2500	115.5	447.93
" 10	Petroleum	.7875	16.6	.4076	58.75	26.93
" 13	"	"	18	.4098	"	27.38
" 14	"	"	16.8	.4032	59.00	26.28
" 17	"	"	16	.4016	"	25.92
" 17	"	"	18.7	.4016	"	26.06
" 21	"	"	18.7	.2538	115.25	27.14
" 15	Benzine	.753	15.7	.3981	59.00	24.26
" 15	"	"	16.6	.3927	"	22.41
" 18	"	"	16	.3891	"	22.45
" 15	Mercury-water		16.6	.3670	"	369.50
" 17	"		18.7	.3663	"	369.37
" 18	"		16	.3636	"	367.87
" 21	"		19	.2272	115.50	361.48
" 22	"		18.7	.2294	115.25	372.30
" 22	"		19.2	.2273	"	364.10
" 24	"		18.4	.2288	"	368.63
" 15	Mercury-alcohol		15.7	.3641	59.00	357.05
" 17	"		16	.3644	"	356.00
" 20	"		18.1	.3650	"	350.97

Changes in Apparatus at Cornell University.

It was found necessary to suspend part of the apparatus in order to get rid of extraneous vibration. The pan holding the liquid, and the fork generating the waves were placed on a slab of iron weighing about 60 pounds. This, in turn, rested on a heavy platform of wood which was suspended from the ceiling by four stout cotton cords. In place of the endless screw, a dividing engine was used to support the telescope, greater accuracy being obtained in measuring λ. A carefully-made silver-on-glass astronomical mirror of 8 inches diameter and 12 feet radius was substituted for the rough lecture mirror. The light was interrupted twice per vibration instead of once as before. This effect was obtained by using the wooden strips at the ends of the fork prongs as before, and cutting a slit in each strip parallel to the axis of the fork so that the light passed through when the fork was at rest, or in its equilibrium position when vibrating. The change which was most convenient was the substitution of a stick of wood for the fork which generated the waves. It was found that the stick, after being clamped to hold it steady, would take up the vibrations as readily as the fork; so the fork was discarded and the glass plate, which generated the waves, was fastened by a suitable device to the end of the stick. Several samples of wood of different kinds and dimensions were tried, the one finally selected being a strip of chestnut 12 inches long, ¾ inch wide, and about ⅛ inch thick. It was clamped at a point near its middle.

METHOD OF CLEANING.

Cleanliness being an essential feature of the experiment, great care was taken in eliminating impurities. The glass and the pan were first cleaned with acid, an alcoholic solution of potash, and running tap water. They were then coated with a moist layer of "Bon Ami" (a commercial article for cleaning glassware) and dried thoroughly. This layer in drying took up any impurities that adhered to the glass, so that when the dishes were thoroughly rubbed with clean cloths the surface was clean. The pan and glasses were then rinsed with running tap water and finally with distilled water. Care was taken in all cases not to let the fingers touch the glass or pan where the liquid was to come in contact.

Mercury was cleaned by pouring it into a bottle containing concentrated sulphuric acid and a pasty layer of mercurous sulphate. The sulphuric acid, being the top layer, took out organic impurities, and water; the next layer of mercurous sulphate acted on metallic impurities present such as compounds of lead, tin, zinc, etc. As these impurities floated on the surface of the mercury, the mercurous sulphate acted readily on them forming zinc-sulphate, lead-sulphate, etc., throwing down metallic mercury. The mercury used was drawn from the bottom of the bottle and found to be free from impurities.

To avoid contamination of the air, each liquid was cleaned just before a measurement was taken by sweeping its surface with a glass slide. This slide could be swept across the pan and held in its final position by means of the pressure against the sides of the pan of strips of rubber attached to the ends of the glass. In this way all the contaminations could be swept into one end and confined there, leaving a clean surface for the waves.

Changes in Method of Measurement.

The telescope was focused successively on three neighboring crests a wave-length apart and readings taken. It was then moved along and focused on the eleventh wave and readings taken for three crests as before. This gives three determinations of ten wave-lengths. At times the waves were not damped out so quickly and more than ten waves could be counted.

Many different samples of glass were tried for generating the waves. In order to get a steady pattern it is necessary that the junction of glass and liquid be a straight line, that is, the liquid should wet the glass. French plate glass was found to work well, but was too heavy for the stick vibrator, the vibrations obtained being too small. A thin piece of plane glass was found to give steady waves and that was used. In February the glass plate vibrator was discarded for a small pointed tube of glass which gave circular waves of a much more steady pattern. The lengths of waves were compared for the two cases, and were found to be the same when the point source was very small.

A new method was used to measure the frequency of the fork. A metal disc 12 inches in diameter and having four slits cut out as shown in Fig. 4 was screwed firmly to the shaft of a small electric motor. The disc was then placed horizontally over the vibrating fork and rotated until the fork prongs appeared to stand still. A speed-indicator was attached to the motor shaft and the number of revolutions in a given time determined by means of a stop-watch. The author was assisted in this determination by Mr. Rands, who read the stop-watch. One of the difficulties was to keep the disc in unison with the fork. This was done by having a little more current than was necessary and slowing the speed of the disc by using the finger as a brake. With a little practice, the author succeeded in having the disc and fork run in unison for any desired time. Three successful measurements were made, the readings being as follows—

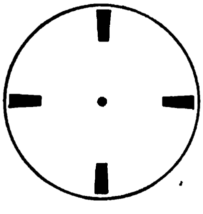

Fig. 4.

1. 3700 revolutions of disc in 5 minutes, 37 seconds.
2. 3600 " " " " 5 " 27.3 "
3. 2100 " " " " 3 " 11 "

giving respectively 10.979, 10.999, and 10.990 revolutions of the disc per second.

The stop-watch was then compared with the standard clock of the Physics Department and found to gain 43.5 seconds in 1 hour and 8 minutes. Appropriate corrections gave the average number of revolutions per second as 11.365, or the number of views through the slits as 4 × 11.365 apparently determining the frequency of the fork to be 45.46. Previous determinations by means of a standard fork had given the frequency as 88.5 approximately, hence the preceding value is one-half the real value. The conclusion[1] was drawn that the fork was seen every *second* vibration, and that its frequency was 8 × 11.365, or 90.92 vibrations per second. The accuracy of the working of the dividing engine was tested by Mr. Barnett[2] and also by the author and found to be correct. Densities and temperatures were determined as usual with standard instruments.

The following table gives the results obtained under the new conditions:

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[1] Rayleigh, Phil. Mag., 16, 53.

[2] Phys. Review, 6, 257.

TABLE II.

Date.	Liquid.	ρ	t	λ	n	T_0
Nov. 23	Distilled water.	1	16.8	.3926	90.92	78.43
Dec. 1	" "	1	15.	.3920	"	77.77
" 1	" "	1	15.	.3923	"	77.95
Feb. 25	" "	1	11.2	.3927	"	77.55
" 25	" "	1	11.4	.3918	"	77.08
" 25	" "	1	11.4	.3912	"	76.72
" 25	" "	1	12.4	.3916	"	77.12
" 25	" "	1	12.2	.3923	"	77.50
Nov. 16	Tap water.	1	10.8	.3911	"	77.59
" 16	" "	1	11.2	.3915	"	76.87
17	" "	1	10.2	.3913	"	76.59
‘ 19	" "	1	8.2	.3916	"	76.27
Feb. 27	" "	1	6.0	.3914	"	75.82
‘ 27	" "	1	6.0	.3912	"	75.88
‘ 27	" "	1	6.0	.3916	"	76.12
Nov. 22	Mercury	13.6	17.5	.3051	"	494.07
" 22	"	"	"	.3042	"	489.55
" 22	"	"	"	.3044	"	490.60
" 22	"	"	"	.3033	"	485.20
" 23	"	"	19.8	.3033	"	487.51
" 23	"	"	"	.3047	"	494.39
" 23	"	"	"	.3038	"	490.07
" 23	"	"	"	.3022	"	482.07
" 23	"	"	"	.3037	"	490.19
" 26	"	"	"	.3026	"	485.10
Dec. 6	"	"	16.	.3002	"	468.65
" 7	"	"	17.5	.3023	"	480.41
" 8	"	"	16.	.3072	"	503.34
" 10	"	"	12.2	.3028	"	477.50
Nov. 23	Mercury-water		19.8	.2719	"	377.96
" 26	"		19.8	.2725	"	380.55
Dec. 6	"		16.	.2702	"	364.12
" 7	"		17.5	.2712	"	373.21
" 8	"		16.	.2706	"	365.77
" 10	"		12.2	.2728	"	374.32
Jan. 26	"		15.	.2730	"	378.88
" 26	"		15.	.2744	"	385.78
Feb. 4	"		11.5	.2720	"	371.96
" 4	"		11.5	.2732	"	376.71
" 12	"		15.5	.2710	"	370.84
" 15	"		14.	.2714	"	371.39
" 18	"		19.4	.2716	"	376.46
" 18	"		19.3	.2706	"	372.24
" 20	"		14.8	.2728	"	377.19
" 20	"		18.4	.2727	"	380.35
" 21	"		16.4	.2731	"	380.57
" 22	"		12.8	.2722	"	373.48
" 19	Mercury-alcohol	.825[1]	13.5	.2697	"	364.27
" 19	"	"	15.	.2697	"	365.02
" 20	"	"	17.5	.2722	"	378.36
" 26	"	"	11.	.2715	"	369.51
" 27	"	"	11.3	.2705	"	366.00

[1] Density of alcohol.

Comparison of Results.

It is first to be noted by the formula

$$T = \rho\left(\frac{n^2\lambda^3}{2\pi} - \frac{g\lambda^2}{4\pi^2}\right)$$

that an error in n is multiplied by two and an error in λ by three approximately in calculating T. The accuracy of the work is best judged then by an inspection of the values of λ, for the error in measuring n is very small. The Cornell measurements (Table II.) are selected for inspection as being more reliable. The measurements of λ on distilled water give an extreme error of less than ⅓ of 1% and a variation from the mean of a little more than ⅙ of 1%. The measurements for mercury are naturally not so good, giving an extreme error of 2⅛% and a variation from the mean of 1⅙%. Mercury-water measurements are more constant, giving an extreme variation of 1½% and a variation from the mean of ⅔ of 1%. The percentage of error is somewhat smaller than these figures indicate, in that wave-lengths for different temperatures are compared.

Comparing the results of Table II. with those of Table I. it is seen that the values for distilled water tensions are nearly the same, the Cornell tensions being about ¾ of a dyne greater. The tension of tap water is nearly as high as that of distilled water. The method pursued in getting these tensions was to rinse the pan thoroughly with running tap water, then draw off enough for measurement, and determine the wave-length as soon as possible. This method of getting a clean liquid by drawing it from the body of the supply rather than by pouring from the surface is in accord with experiments of Lord Rayleigh[1] and also of Mr. T. P. Hall.[2] Cornell measurements of mercury tensions give higher results throughout, due, without doubt, to the precautions taken in cleaning the surface and to the method of eliminating impurities. The values for mercury-water tensions show less difference than mercury-air tensions. The best interpretation here seems to be that most of the contamination from the air is probably moisture, so that water placed in contact with two samples of mercury—one exposed to the air and the other not—would give nearly the same interfacial tensions. This interpretation is shown by the results of Table II. The mercury-water tensions taken in November were on mercury previously exposed to the air, while the measurements in February were on a mercury-water surface where the mercury was drawn off *under* water, and not exposed at all to the air. The measurements in the two cases give practically the same results. Comparison of mercury-alcohol tensions show Cornell measurements to give higher results. This is probably due, as before stated, to better precautions in matter of cleanliness. The alcohol used at Cornell was distilled from the best commercial alcohol obtainable. The mercury used at the University of California was distilled in an ordinary vacuum still and filtered through clean cheese-cloth to remove motes from its surface, while the mercury used at Cornell was cleaned with sulphuric acid and mercurous sulphate, and was drawn off fresh for each measurement.

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[1] Phil. Mag., (5), 33, p. 363.

[2] Phil. Mag., (5), 36, pp. 411–412.

Other Interfacial Tensions.

Attempts have been made to measure surface tensions between mercury-petroleum and mercury-benzine, but a contaminating film was formed in each instance, so that no measurements were carried out.

Measurements have been taken giving tensions between water-petroleum and water-benzole. The results first obtained showed great variation. Several difficulties prevented accurate measurements being taken, first, a strong damping of the waves so that only four or five waves could be counted; and second, an irregularity in the wave pattern causing a variation in the measurement of the wave-length. (See Fig. 10.) It has already been stated that to get a steady pattern of the waves the line of junction of glass and liquid must be a straight line. This condition was not obtained with a water-petroleum surface when a plane glass vibrator was used—the result each time being a "crinkly" line. Later, however, a steady wave pattern was obtained by using a sharp-pointed glass tube as the source of disturbance. A third difficulty was experienced because of an insufficient illumination of the interfacial waves, the index of refraction of water being so nearly that of oil that but little light was reflected from their plane of separation.

To remedy this trouble an incandescent lamp of 100 candle-power was substituted for the one having 16 candle-power, and a mirror of shorter focus was substituted for the astronomical mirror. Changing the mirrors introduced a new source of error in that the new mirror, being roughly made, did not reflect the light in parallel rays. However, it was necessary to have more illumination in order to see the waves distinctly enough for measurement, so the change was made.

The usual precautions in regard to cleanliness were observed, the glasses and porcelain dish being cleaned with a concentrated nitric acid and a strong alcoholic solution of potash, besides being thoroughly rinsed with running tap-water and finally with distilled water. The benzole, petroleum and turpentine used were the best commercial article, and no attempt was made to purify them. Each liquid was placed in a thoroughly clean separatory funnel, and was drawn off from the bottom to prevent surface contamination.

Measurements were taken under these conditions, the liquids being arranged as shown in Fig. 2. Results are given in Table III.

TABLE III.

Date.	Liquids.	ρ	t	λ	n	T_0
April 2	Water-benzole.	.753	17.9	.2460	90.92	35.15
" 2	" "	"	15.6	.2380	"	31.75
" 3	" "	"	15.5	.2400	"	32.47
Jan. 22	Water-petroleum.	.787	17	.2428	"	34.36
March 2	" "	"	17	.2445	"	35.39
April 5	" "	"	19	.2420	"	34.18
" 5	" "	"	14.8	.2465	"	36.11
" 9	" "	"	17	.2480	"	36.79
" 9	" "	"	17	.2450	"	35.46

The density, ρ, here indicates the density of the lighter liquid, the density of water being taken as 1. The measurements of April 5 and 9 for water-petroleum were taken on petroleum that had been previously shaken with mercury to remove sulphur compounds. The results obtained show greater variation than do measurements for the tension between a single liquid and air. This is to be expected when the existing difficulties are considered. Each result recorded is the average of three or more measurements. Benzole-water tensions were obtained to ascertain if a definite compound, such as benzole, would give a more constant tension with water than a mixture like petroleum. Each set of measurements has about the same range of variations so that by this method one tension is no more constant than the other.

Verification of Results.

These results were verified by two other methods. The first method involved the use of the Jolly balance. Surface tension was calculated by measuring the pull of a liquid film on the spring of the balance. The film was formed by means of a wire rectangle which was first immersed below the surface of the liquid and then drawn up by the spring. Two readings were taken, one when the rectangle was submerged and the second when the liquid film broke. The difference between these readings divided by twice the width of the rectangle and multiplied by the force in dynes necessary to stretch the spring one division of the scale gave the surface tension.

The second method was similar in principle. The pull of a suspended liquid film was measured by the sucking force of a coil of wire carrying a current.[1] (See Fig. 5.) *MN* represents the coil of wire which is wound about the small glass tube *AB*. *CB* is a bit of No. 26 soft iron wire, to which is soldered the piece of No. 33 copper wire, *CA* and the suspended rectangle *DE*. This core was hung inside the small glass tube, and prevented from falling by the small globule of solder at *A*, though a free upward movement was allowed.

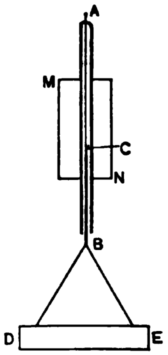

Fig. 5.

Knipp found that the current necessary to raise the rectangle was proportional to the surface tension of the liquid used. The plan followed by the author was to immerse the rectangle in water and note the current necessary to raise the core. The rectangle was then raised until its upper edge was just below the surface of the liquid. The current was turned on, causing the rectangle to rise and form a film which broke after it had been stretched sufficiently.

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[1] Knipp, Phys. Review, 11, 129, 1900.

The current strength was noted at this moment of breaking. The difference between the two readings taken was assumed to be proportional to the surface tension of water. The rectangle was again submerged just below the water surface and another liquid, such as petroleum, poured on the water; the current was turned on and its strength noted as the interfacial film broke. Finally the tension of the upper liquid was determined in the same way as that of water.

The glass beakers used to hold the liquids were cleaned as usual with alcohol, potash, nitric acid and water. The wire rectangle was of brass and was cleaned by the action of acid, all the outside layer being eaten off and the new surface thoroughly rinsed with water. It was found that a thin sheet of copper or platinum foil could be used in place of the brass wire rectangle, the results in each case being practically the same. Table IV. shows the results obtained.

TABLE IV.

Method used.	**Water Tension.**	**Water-petroleum Tension.**	**Petroleum Tension.**	**Water Tension.**	**Water-benzole Tension.**	**Benzole Tension.**
Jolly balance.	75.73 73.99 72.30	44.74 43.89 42.49	28.10 28.90 25.36	75.1 74.9	35.51 36.20	27.2 30.6
Coil of wire.	75 75 75	41.4 38.3 33.8	27.2 29.5 28.7			

Interfacial tensions between water and benzole are the same as values obtained by ripples within errors of observation of the Jolly balance method. The seeming discrepancy in the interfacial tensions between water and petroleum puzzled the author for some time until a solution of the difficulty was found in an article by Mr. T. P. Hall,[1] in which he states, concerning the formation of liquid films, "Even when the bar is excessively thin a distinct maximum of weight is noticeable as the frame is raised, just before the true double film is formed. The bar must be raised from five to ten millimeters before a true film is formed, the tension not being correctly found at a less height."

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[1] Phil. Mag. (5), 36, 385.

The height to which the rectangle was raised before the interfacial film broke was about 0.3 cm. as nearly as the author can remember from observation; therefore, according to Mr. Hall, the measurement should be high, which harmonizes with the results found. Mr. Hall shows that the tension can be found in terms of this maximum weight. The author has modified Mr. Hall's method to suit the present case and has found a verification of the measurements taken on ripple waves. The following paragraphs give details.

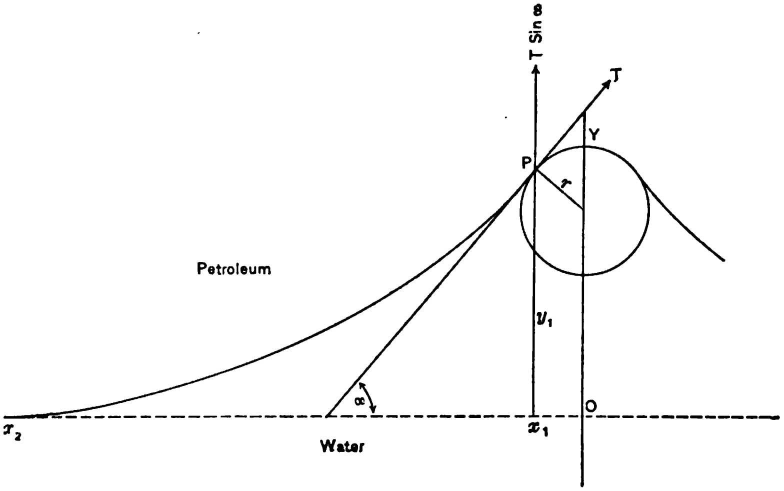

Fig. 6.

Fig. 6. is a vertical cross-section of the liquids, the circle representing the upper bar of the wire rectangle and Px_2 the line of separation of the two liquids. The weight of the mass above the interfacial level is desired. Taking a slice of unit thickness the weight of the mass from x_1 to x_2 is equal to the vertical component of the tension at the point P. The weight of the strip $OYPx_1$, may be taken with sufficient accuracy to be equal to the weight of the wire (immersed in water) plus $y(r \sin a)g \cdot (\rho_1 - \rho_2)$ where r is the radius of the wire, g the acceleration of gravity, ρ_1 the density of water and ρ_2 the density of petroleum. Thus the entire weight of the lifted mass

$$W = \omega + 2\,T \sin a + 2rgy(\rho_1 - \rho_2) \sin a$$

where ω is the weight of the brass wire when immersed in water.

In the experimental work this weight, w, was accounted for by subtracting the first reading from the second, so that there is left to calculate then only

$$W = [T + ryg(\rho_1 - \rho_2)]\ 2 \sin a.$$

It yet remains to find an expreseion for sin a. It has already been stated that the vertical component of the tension supports the liquid, of unit thickness, included in the boundary $x_2\ P_1\ x_1$ thus

$$T \sin a = g(\rho_1 - \rho_2) \int_{-\infty}^{\infty} y dx$$

from which

$$\frac{dx}{da} = \frac{T \cos a}{gy(\rho_1 - \rho_2)} = \frac{c^2}{4y} \cos a$$

where

$$c_2 = \frac{4T}{g(\rho_1 - \rho_2)}.$$

Further, as $\tan a = \dfrac{dy}{dx}$

$$\frac{dy}{da} = \frac{dy}{dx} \cdot \frac{dx}{da} = \tan a \cdot \frac{c^2}{4y} \cos a = \frac{c^2}{4y} \sin a$$

integrating

$$\cos a = \frac{c^2 - 2y^2}{c^2}$$

and

$$\sin a = \frac{2y}{c^2} \sqrt{c^2 - y^2}.$$

Substituting this value in the original equation

$$W = [T + ryg(\rho_1 - \rho_2)] \frac{4y}{c^2} \sqrt{c^2 - y^2}.$$

Assuming $T = 35$ dynes, the average value found by method of ripples, and substituting values for the other quantities, $y = 0.3$ cm. (by observation), $g = 980$ dynes, $\rho_1 = 1$, $\rho_2 = 0.8$, $r = 0.02$ cm.

$$W = 48.00 \text{ dynes.}$$

The observed maximum value for W is 44.7 dynes, which justifies approximately the assumption of 35 dynes for the interfacial tension of water petroleum. A probable explanation of the measurements giving less than 44 dynes is suggested by a consideration of the method of measuring. The rectangular was kept wet with water until petroleum was poured on the water surface. The rectangle was then raised until the interfacial film broke, leaving the rectangle immersed in petroleum and probably partially wet by it. This first measurement was usually high. On again lowering the rectangle and repeating the measurement of the interfacial film, the tension was usually found to be less. Further repetitions gave still lower tensions until a minimum value was reached which was approximately the value obtained by method of ripple waves. These considerations lead strongly to the supposition that a true film was formed after the rectangle was immersed in the petroleum.

Ripple Waves.

The author has devoted some time to a study of the waves themselves and presents here some of the results obtained.

The photograph reproduced in Fig. 4 gives a general idea of the liquid surface when ripples are steadily maintained. The photograph was taken by Vincent's method.[1] The dark cross in the center shows the tuning fork prong and the vibrating plate, the meniscus about the plate making it appear thicker than it really is. The fork and waves are smaller than their real size. The ends of the glass plate act as point sources of disturbance and send out circular waves which interfere and form, as Vincent has pointed out, a family of ellipses and a family of hyperbolas. The author has been able to distinguish these at times by viewing the surface at a favorable angle of incidence. The circular waves interfere also with the straight parallel waves forming a family of parabolas which have their foci at the point source of disturbance. The circular waves in the upper right hand corner were caused by some extraneous vibration of the pan just as the negative was exposed.

Fig. 5 is also a reproduction of a photograph of mercury waves and shows the effect of extraneous disturbances, the pan being placed directly on the floor instead of cushioned as before.

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[1] Phil. Mag., 45, 191.

Figs. 6 and 7 are from two photographs taken by means of reflected light, the camera being placed in the position usually occupied by the telescope. A large plano-convex lens of six inches diameter was used to bring the light to a focus at the camera stop. The time of exposure for the photograph of the oil-water waves was nearly ten minutes. The distinctness of the crests furnishes an evidence of the unison of the frequencies of the interrupted light and the waves. The strong damping of waves already mentioned is here shown.

The amplitude of the waves is very small. To get an approximate idea of the size of the waves the author measured the amplitude of the fork which generated the waves. This was done by vibrating the fork more vigorously than usual and observing its motion by means of interrupted light. The frequency of the light flashes was made slightly different from that of the fork so that the latter appeared to move slowly. The magnitude of its excursion was measured by means of a traveling microscope and found to be .0116 cm. Much difficulty was experienced at first in focussing on a definite point of the fork. The device that was finally successful was to fasten a needle to the fork with a bit of wax and observe it through the microscope when the field of the latter was made half dark by pasting a piece of paper over half the aperture. Fig. 11 shows the two positions of the needle when measurements were taken. The reading for position *A* was taken when the fork was at rest, the position of the needle being accurately shown by the narrow band of light *DC*. The fork was then vibrated and a reading taken for the position of extreme vibration at *A′*. The magnitude of the excursion, as already stated, was found to be .0116 cm. The fork's usual amplitude may safely be taken as one-half the amplitude for this case, thus giving the maximum amplitude of the waves generated by the fork as .0058 cm. or $\frac{1}{16}$ of a millimeter.

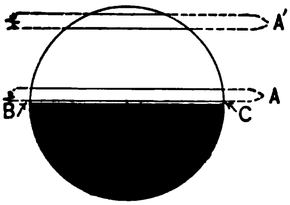

Fig. 11.

The waves die down due to the viscosity of the liquid according to the usual logarithmic decrement. This action of the waves gave

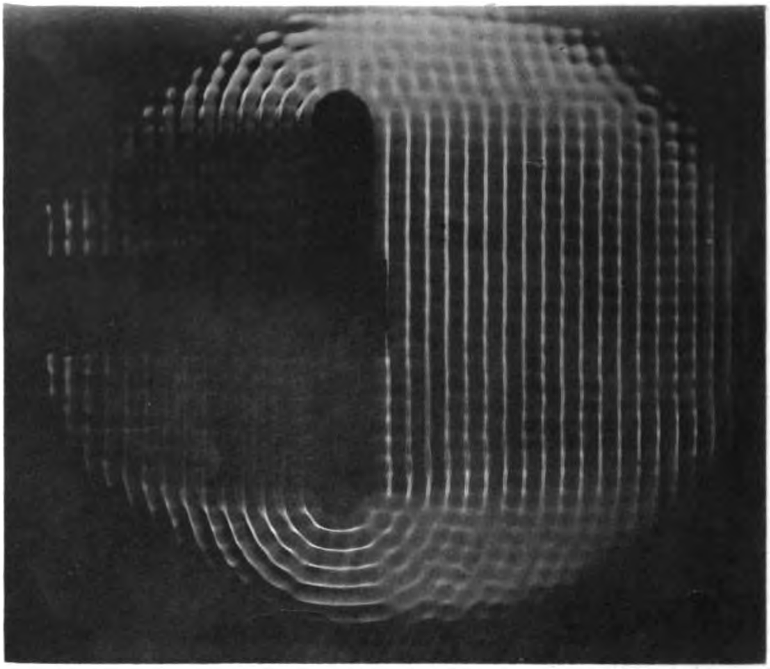

FIG 7.

Photograph of mercury waves.

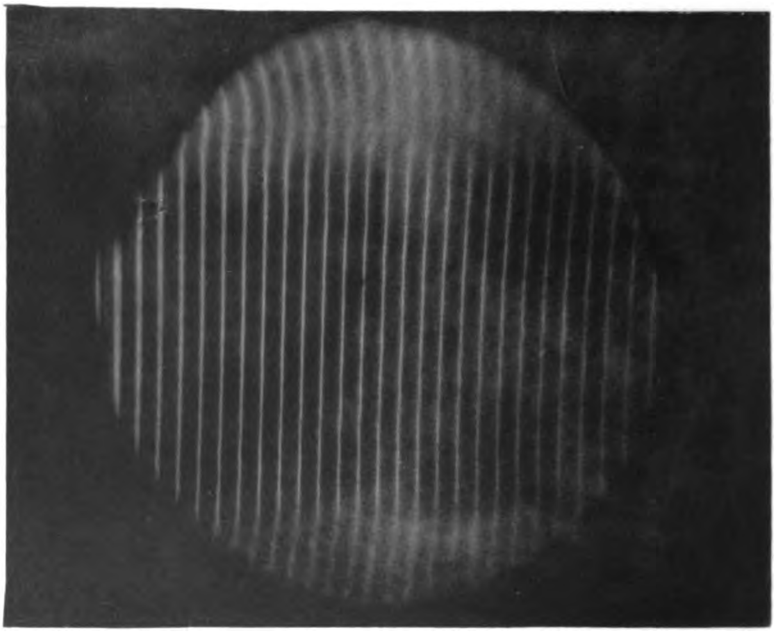

FIG 9.

Waves at the interface of mercury and water.

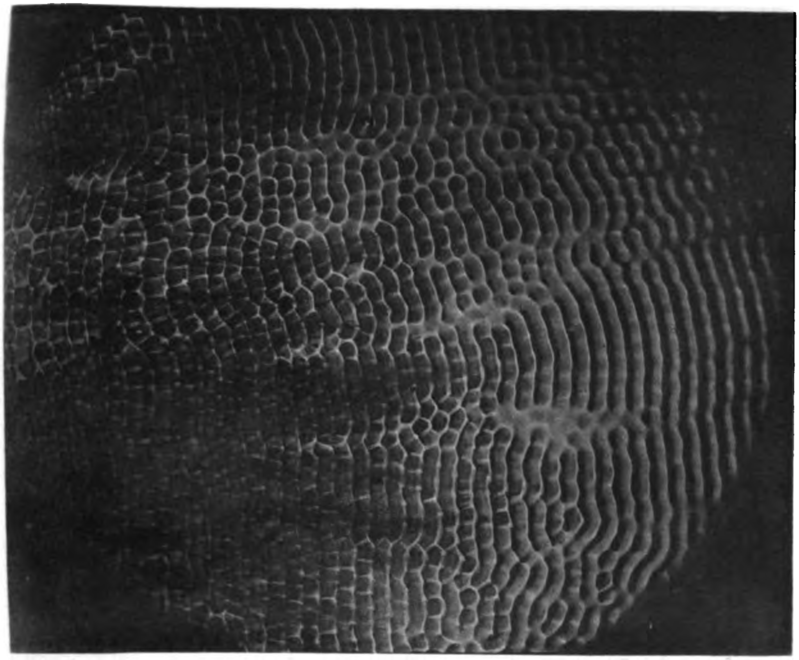

FIG 8.

Mercury waves.

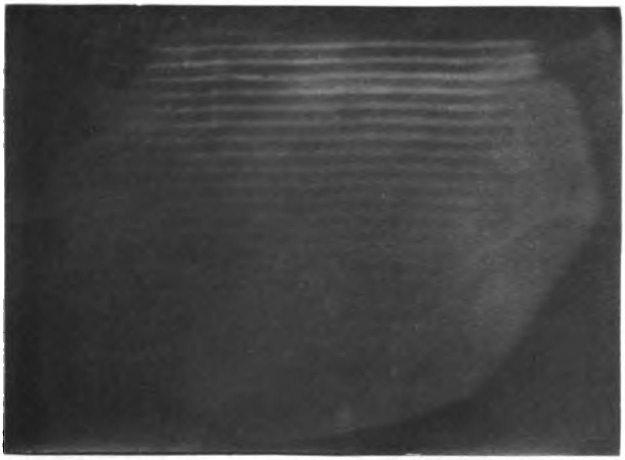

FIG 10.

Interfacial waves, between oil and water.

some trouble in taking measurements of the wave-length, for the telescope would get out of focus as it was moved along. The following diagram (Fig. 12) explains the difficulty more clearly.

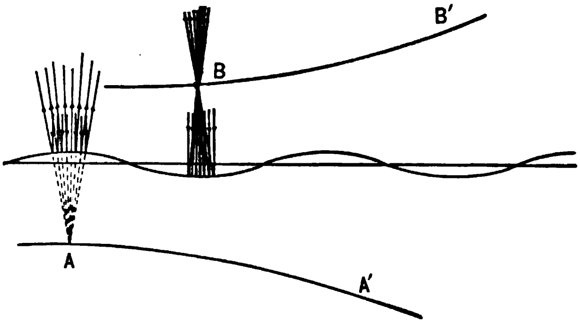

Fig. 12.

The light rays are parallel and, as they strike each crest, are reflected as they would be from a convex mirror, appearing to come from the foci A, A', A'', etc. Similarly, on striking a hollow, the reflection takes place as it would from a concave mirror, bringing the light to a focus at B, B', B'', etc., as only a small part of the reflected light enters the telescope, the waves appear as narrow bands of light with dark spaces between. The waves in dying down become flatter and the foci consequently further removed from the surface of the liquid, so that the telescope which moves parallel to the surface soon loses the sharp focus of the waves. The curves of the foci are shown in Fig. 13.

The surface of the liquid is represented by the x-axis, the vibrating plate being at the origin. The telescope moves along the line $y = 75$ cm. The abscissæ represent distances from the vibrator on the surface, and the ordinates the distances of foci from the surface. The curve for foci of crests is below the surface and for foci of hollows above. The two curves are symmetrical so far as traced. The method of locating the points on the curve was as follows: move the telescope to a position (4, 75) (say) and focus on a crest; turn the telescope away from the surface, keeping the same focus, then bring an object into focus—a small stick of wood was used—and measure the distance from the telescope to the stick. This distance is the distance from the telescope to the focus. In this way both curves were plotted.

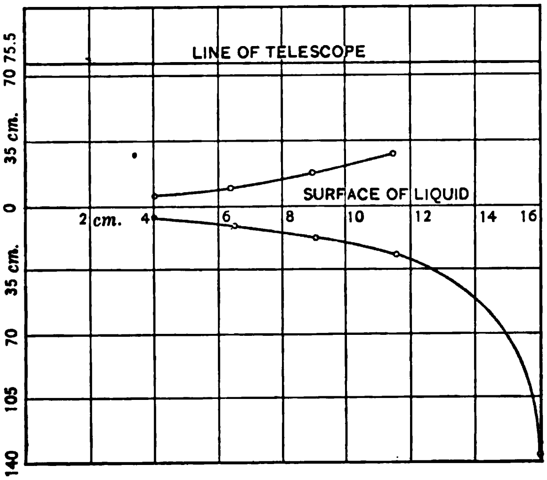

Fig. 13.

In conclusion, the author desires to express his thanks to the members of the Physics Department of the University of California for courtesies shown, and especially to Professor Slate for his advice and encouragement during the beginning of the work. The author is also grateful to Professor Nichols and staff of Cornell University for valuable suggestions given and for the liberal use of apparatus and facilities. Diagrams of apparatus were kindly drawn by Mr. A. V. Saph.

The Physical Laboratory of Cornell University, March, 1901.

AN IMPROVED METHOD OF RATING TUNING FORKS.

By John O. Reed.

ALTHOUGH the tuning fork has long been used as a means of measuring small intervals of time, yet a cheap, convenient and accurate method of rating the fork has remained a thing much to be desired. Of the various methods proposed, the most successful have generally employed the stroboscopic principle in some form or other. Of these the method first described by Michelson[1] is unquestionably the most simple and convenient, although attended with experimental difficulties which materially limit its usefulness and detract from the accuracy of which it is otherwise capable. In the effort to obviate these difficulties the writer has resorted to a number of devices, some of which are, it is thought, sufficiently successful to warrant their description as a distinct method.

In the method as described by Michelson, the standard fork is compared with an auxiliary fork by counting beats; the auxiliary fork is driven electrically and is furnished with a mirror, in which is viewed the flash of a Geissler tube; this tube is actuated by an induction coil whose primary circuit is periodically closed by a pendulum of known period. When the fork is at rest the flashes are seen at one place and appear at rest. When the fork is made to vibrate the flashes form a stroboscopic procession back and forth across the field of view, and from the number of flashes needed to complete the cycle the frequency of the fork is readily determined, provided its value is approximately known.

The difficulty in securing exact periodicity in the flashes of the tube forms a most serious obstacle in the use of the method, as originally described. Michelson points out that if the intervals between the flashes differ by 0.002 of a second, the method becomes impossible for a fork of frequency 128 v. s. He accordingly devotes much attention to the mercury contact in order to make the flashes as nearly isochronous as possible. The sources of error due to this contact are numerous. First, the mercury globule must be exactly in the center of the arc of the pendulum, an adjustment difficult to get and troublesome to maintain. Again if the globule have any appreciable thickness in the direction of the moving point, there is an interval of time between the make and break of the primary current, sufficient to give rise to a system of double flashes of varying intensity. These become extremely confusing to the observer trying to follow the stroboscopic procession across the field of view, and in many cases it is impossible to decide in which direction the flashes are moving. Oscillatory discharges of the coil are also possible, and the flashes become very complex and misleading.

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[1] A. A. Michelson, Philos. Magazine, Vol. 15 (5), p. 84, 1883.

By properly adjusting the resistances in the primary and secondary circuits, and by making the globule thin and flat, the abovementioned difficulties may be largely obviated, but there remain more serious objections; first, the time of discharge of the coil through the tube is not a definite interval, much less is it amenable to control or regulation; again, the mercury globule soon becomes coated with a film of oxide, even when weak currents are used, and this film drags after the contact point, forming a minute tail which prolongs the time of break in some cases as much as one or two thousandths of a second and is always irregular and uncertain in its action. Now, the fundamental assumption in the application of the stroboscopic method is that the intermittent illumination shall be strictly isochronous and that the time of illumination shall be vanishingly small as compared with the period of the motion to be studied, in order that the body may not move sensibly during the illumination. Consequently an illumination that would be entirely satisfactory for a fork of frequency 64, would be inadequate for work upon a fork of frequency 128 or 192, since in the latter case the flashes would be spread out into broad bands of three times the width of the same flashes as seen in the mirror of fork 64.

It is evident, therefore, that a system of illumination intended for use in stroboscopic work must not only be isochronous to any required degree of accuracy, but if it is to find general application, it must also be entirely under control as regards the duration of the illumination, and this duration must be capable of adjustment within considerable limits. From the above considerations it is clear that the flash of a Geissler tube is but poorly adapted to the stroboscopic study of vibratory motions of even moderate frequency, and a new source of intermittent illumination must be provided. A satisfactory substitute is found in the following arrangement.

A rod R_1, 8 mm. in diameter and 100 cm. long, hung from two short pieces of clock spring, aa, carries on its lower end a large lens-shaped mass of lead, L, and four adjustable weights 1, 2, 3, 4, the whole forming a free pendulum of adjustable period. Below the middle of the rod is clamped a ring to which is attached a shortarm l, bearing at its outer end a small needle n. Against this rests a short piece of fine glass tube t, about 0.1 mm. in diameter and attached normally to a vertical axis p which turns in point centers and carries a plane mirror m. As the pendulum swings in a plane normal to the plane of the paper, the mirror is caused to rotate about the vertical axis p, through a relatively large arc whose angular amplitude A, is given in terms of a, the angular amplitude of the pendulum, by the relation $aR = Ar$ or $A = aR/r$, where R and r represent the effective radii of motion of the pendulum and mirror respectively at the point of contact of the tube and needle. The tube is held against the needle by means of a small drop of oil at

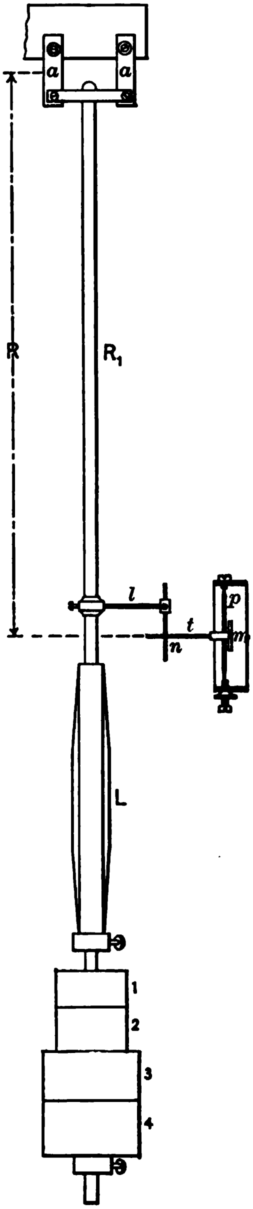

Fig. 1.

the point of contact, the viscosity of the oil being sufficient to carry the mirror on its return swing.

If now there be thrown upon the mirror *m* a beam of light from any convenient source, we have a moving spot of light which may be given any desired linear velocity, and whose successive vibrations are isochronous to a high degree of accuracy. The source of light is a brightly illuminated slit, shown at *s* (Fig. 2) from which the light is focussed at *s′* by the lens *l* after reflection at the mirror *m*. *T* is an Abbé autocollimating telescope, having a totally reflecting prism in the focal plane of the eyepiece, by means of which the light entering the window at *s′* is thrown directly into the axis of the telescope and leaves the objective in parallel rays. Directly in front of the prism is an adjustable slit *s″* (not shown in the figure), thus allowing the telescope to serve both as collimator and observing telescope. The parallel rays from the telescope strike the mirror *m′* normally, and return to form an image of the slit *s″* in the focal plane of the telescope. So long as both pendulum and fork are at rest there is seen in the field of the telescope a single bright image of the slit. If the pendulum be set in motion this image flashes brightly each time the image *s′* sweeps past the small window in the telescope, the duration of the flash with a given pendulum depending upon the width of the window, the width of the image *s′*, the distance *ms′*, and the ratio *R*/*r*.

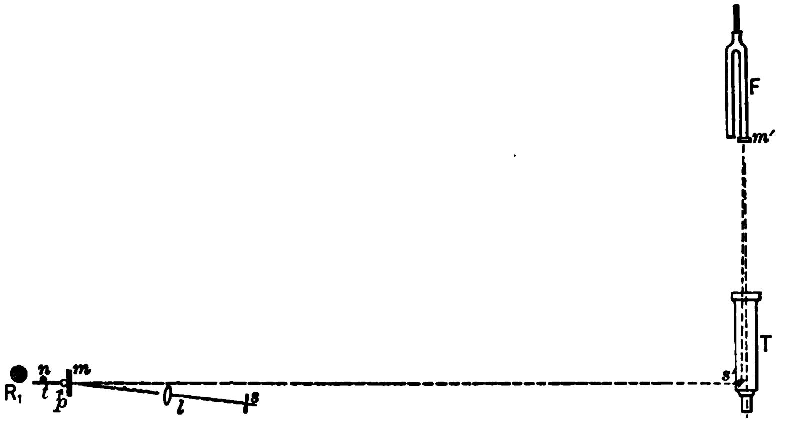

Fig. 2.

When the fork is set in motion the image in the telescope becomes a stroboscopic procession of images moving across the field, each one so sharp and distinct that coincidences with the cross hair of the telescope may be observed or approximate coincidences estimated to a fifth of the width of a slit image without difficulty.

In practice the free pendulum is rated in terms of the standard clock at the same time that the observations are made on the fork, one observer being able to carry on both sets of readings by working alternately upon first the one and then the other. By determining the period of the pendulum at the time of the observations upon the fork, corrections for effects of temperature upon the pendulum are obviated. The rating is effected by the method of coincidences as employed by Mendenhall[1] in his work upon the determination of *g*. The coincidences are observed by viewing the flash of a Geissler tube marking seconds, in a system of mirrors, one fixed and the other attached to the free pendulum. The "coincidence" occurs when the composite image of the flash appears as an unbroken line. To this end the pendulum carries a small mirror about 3 cm. wide and 6 cm. long, and near it in the same vertical plane, is placed a fixed mirror of the same size, so adjusted that the image of the capillary part of the Geissler tube appears as one straight piece when seen in the mirrors with the pendulum at rest. It is necessary to take the coincidences with the pendulum of the clock always going in the same direction, in order to avoid the error due to any slight eccentricity in the position of the mercury globule.

Under ordinary circumstances the period of the pendulum can be determined to hundred-thousandths of a second in twenty minutes, usually not more than five coincidences being necessary. During the intervening intervals a sufficient number of cycles of the fork can be counted to give all the data needed to determine its frequency so that the entire process may be completed in half an hour. In laboratory practice it is customary to require the student to make three determinations and take the mean. For this purpose three different pendulums are arranged by making suitable combinations of the adjustable weights 1, 2, 3, 4 shown in Fig. 1, so that for each pendulum a workable cycle of flashes from the fork may be secured. The best results are obtained by using cycles of not less than five nor more than ten flashes per cycle. The computation is as follows:

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[1] T. C. Mendenhall, Am. Jour. of Science, Vol. 43, p. 85, 1892.

Let N be the frequency of the fork to be rated.

Let t_1, t_2, t_3 be the periods of the pendulums 1, 2, 3, where $t_1 < t_2 < t_3$.

Let n_1, n_2, n_3 be, to the nearest integer, the number of complete vibrations made by the fork in times t_1, t_2, t_3.

Let a_1, a_2, a_3 be the number of flashes per cycle made by the fork with pendulums 1, 2, 3; where $5 < a < 10$.

Let c_1, c_2, c_3 be the reciprocals of a_1, a_2, a_3 respectively. Then

$$Nt_1 = n_1 \pm c_1$$
$$Nt_2 = n_2 \pm c_2$$
$$Nt_3 = n_3 \pm c_3.$$

If now $(t_3 - t_1) < \frac{1}{2N}$ then $n_1 = n_2 = n_3 = n$, and we have

$$N = \frac{n \pm c_1}{t_1} = \frac{n \pm c_2}{t_2} = \frac{n \pm c_3}{t_3}.$$

If N be approximately known, *i. e.*, to the nearest integer, then n may be set equal to Nt. If N be wholly unknown the graphical method may be employed to determine its approximate value.

The proper sign to be chosen for c in the three equations is shown from the following consideration: The free pendulum as it swings decreases in period very slightly as the amplitude decreases; this decrease in period is evidenced by a slight but unmistakable variation in a, the number of flashes per cycle in each individual case, and consequently by a corresponding variation in c, the fraction of a swing by which the fork exceeds or falls short of an integral number of swings in time t. Now as t decreases this excess will diminish or the deficit will increase; therefore if a is found to increase during the experiment c is positive; if a is found to decrease, c is negative.

In making a determination the apparatus is first carefully adjusted until the spot of light falls exactly on the window of the telescope when the pendulum is at rest, and the image of the slit is very bright. The pendulum is then started, the fork set in vibration and the cycle of flashes roughly determined. If necessary the pendulum must be adjusted by moving the small weights at the lower end until the number of flashes per cycle lies between 5 and 10. For convenience of reference a small sketch of the pendulum showing position of weights is usually appended. The pendulum observations are then started by taking three or four coincidences in quick succession, to get its cycle roughly, after which the coincidences may be taken in groups of three at intervals of five minutes or more as the work proceeds. Only one of each group is used, the others being merely to insure against possible failure to keep track of the pendulum. In the intervals between the observations on the pendulum the fork is bowed and the coincidence of the flash with the cross wire of the telescope awaited; when this occurs the flashes are counted continuously, the observer making note of the coincidences, underscoring those especially sharp, as long as the fork will run, or until the images can no longer be seen sharply separated. The fork is bowed again and the observations repeated. In the computation the mean value of *a* is to be taken, and exceptionally sharp coincidences are to be assigned greater relative importance in determining the value of *a*; from this the value of *c* is computed.

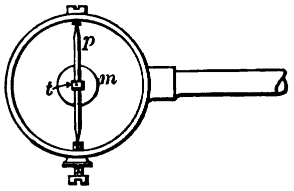

Fig. 3.

It is well to note the time of beginning each set of observations upon the fork, as in this way the varying value of *a* may be readily followed.

The following example of a complete determination will render the method clear:

Pendulum gaining. 6 *in* 64; *better* 14 *in* 150. *January* 2, 1898.

Transits.	**Seconds.**	**Vibrations.**	**Period.**	**Fork bowed.**
3 02 11				6<a<7
03 15	64	70	0.914	nearer 6.
05 45				
07 11	300	328	0.9146	*3*, *07*, *11*
14 21				6, 44, 88
15 25				
16 51	880	962	0.91476	6, 44, *63*, 88
29 01	1610	1760	0.91477	
30 27				6, 25, 44, 88
31 31				....
35 49	2018	2206	0.914778	*3*, *16*, *51*
38 19				6, *31*, 43,
39 45	2254	2464	0.914773	86
43 41				6, *37*, *74*
45 07	2676	2816	0.914773	6, *43*, 49, 98

$t_1 = 0.91477$ sec.

Computation of a_1.

Flashes.	**Cycles.**	*a*.	
1st set. 44	7	6.285	$6.285 \times 9 = 56.565$
63	10	6.300	6.300
25	4	6.25	6.250
			11)69.115
			$a = 6.283$
2d set. 31	5	6.200	6.200
43	7	6.1428	$6.1428 \times 4 = 24.5712$
49	8	6.125	$6.125 \times 3 = 18.375$
37	6	6.166	$6.1666 \times 3 = 18.4998$
			11)67.6460
			$a = 6.1487$
			Mean $a_1 = 6.2158$

a_1 decreasing, hence c_1 is negative.

$c_1 = -\ 0.16089$

$n = 30.$

$t_1 = 0.91477$ sec.

$$N = \frac{29.83911}{0.91477} = 32.619.$$

A second fork gave for ten different determinations, by different persons on different days, the following values:

Temperature.	N_t	N_{20}
13.0°	32.493	32.468
17.5°	32.475	32.466
17.7°	32.473	32.465
18.8°	32.472	32.468
19.5°	32.469	32.467
21.0°	32.464	32.467
22.7°	32.458	32.468
23.0°	32.457	32.469
23.0°	32.455	32.467
23.4°	32.456	32.469

Reduction to 20° C. has been made by the use of Koenig's formula,[1] $\triangle N = \frac{-N}{8943}$ per degree centigrade.

For forks of higher frequency the requirements are greater accuracy in the adjustment of the light upon the telescope slit when the pendulum is at rest, more powerful illumination of the slit and greater velocity of the moving image. The last requirement is met by increasing the ratio R/r, and the distance ms'. With a slit illuminated by an acetylene flame or an arc light, no difficulty is experienced in reducing the duration of the flash to 0.00001 of a second, a period sufficiently short to show the slit image in the telescope, sharp and clear, when reflected from the mirror of a fork making 256 double vibrations per second, even in the middle of its swing. This is readily seen from the following considerations: Assume the amplitude of the motion of the slit image as seen in the telescope to be 5 mm.; then the maximum velocity of the image is 8,050 mm. per second. Also assuming the limit of the resolving power of the eye to be 0.073 mm. at the distance of distinct vision, we have for the duration of the flash

$$t = \frac{0.073}{8050} = 0.000009 \text{ second.}$$

In case it is not desirable to attach a mirror to the fork under investigation, Michelson's second method may be applied; that is the flashes from the pendulum may be received directly into the objec-

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[1] Koenig, Wied. Annalen, 1880, N. F., 9, p. 413.

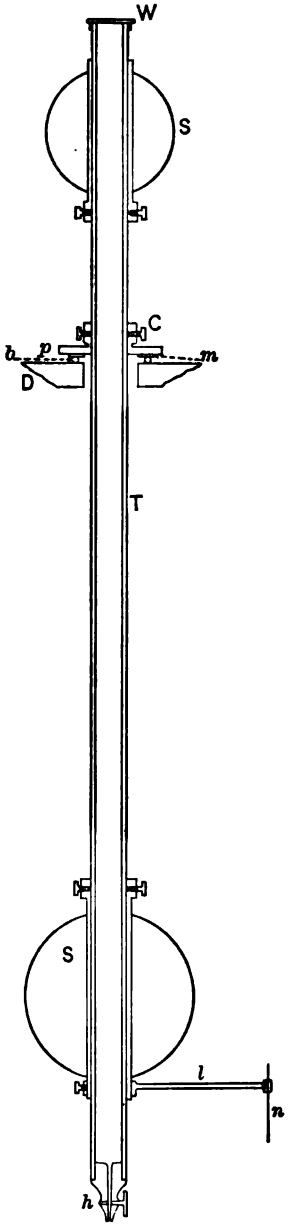

Fig. 4.

tive of a low power microscope in front of which is placed the fork with one prong sharply focussed so as to fill half the field when at rest. The flashes will then give a stroboscopic procession of shadows instead of images of the slit as before. Even by this method forks may be rated, whose frequency would entirely preclude the use of the Geissler tube.

For the purposes of an investigation of which an account will appear later, it became necessary to vary the period of the flashes continuously and by any desired amount. To this end a special form of free pendulum was devised, the main features of which are shown in Fig. 4.[1] A piece of bicycle tubing *T*, 2.5 cm. in diameter and 100 cm. long is fitted with an adjustable collar *C*, to which is attached a brass plate *p*, 7 mm. thick. On the under side of this plate are fastened two small plates *mm'* of hardened steel, each 3 mm. thick and having their under surfaces ground plane. These plates rest upon two small bicycle balls $\frac{3}{32}$ of an inch in diameter, which in turn rest in two small depressions in the bed plate *D*. At either end of the tube *T* are clamped spheres of lead *SS'* of 7 and 10 kilograms mass respectively. By means of set screws these spheres may be given any desired position on the tube.

At the lower end of the tube is fitted a steel plug and stopcock *h*, by means of which a quantity of mercury held in the tube may be varied at will. A small collar holds the horizontal arm and the needle for actuating the rotating mirror as shown in Fig. 1. The bed plate *D* rests upon three short pointed feet which are held in place upon a steel plate on the supporting frame by the familiar hole and slot arrangement. The whole is supported by a rigid frame of suitable height, firmly clamped to a stone pier.

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[1] This pendulum was made by Mr. R. H. Miller, instrument maker to the university, to whose practical suggestions and skillful workmanship much of its admirable performance is due.

By adjusting the relative positions of the supporting plate and the two lead spheres, the period of the pendulum may be varied within wide limits. In practice the period is kept approximately either 0.5 second or one second for a single swing. In the latter case the system with rotating mirror attached will vibrate about three hours and still retain sufficient amplitude to permit of satisfactory observations. With smaller balls the duration of the motion may be made even longer.

As will readily be seen the variation of the period in order to obtain a workable cycle of flashes may now be made to any degree of accuracy and *also while the pendulum is in motion.* To this end mercury is poured into the tube until the period is slightly longer than desired. The apparatus being adjusted the pendulum is set in motion and the cycle observed. If not satisfactory a tap of the pencil upon the stopcock *h*, allows a fine stream of mercury to flow out into a convenient receptacle, and the flashes are observed until a workable cycle is secured when a second tap of the pencil closes the stopcock. In this way the pendulum may be "*tuned*" to any desired period with great accuracy. The enclosed column of mercury serves the additional purpose of rendering the pendulum much less sensitive to changes of temperature, and in case it were deemed desirable, practically complete compensation could be secured in this way. In such case the variation of the period may be effected by placing small weights upon the small cap *w*, at the upper end of the pendulum.

By the use of the above pendulum the following values were sesured for the frequency of a fork marked 512 v. s. using the mirror and flash method.

Temperature.	N_t	N_{20}
20.2°	256.019	256.025
21.0°	255.993	256.022
22.3°	255.960	256.026
20.8°	255.995	256.018
23.0°	255.934	256.020

From the above values it is evident that the method is applicable through quite a range of frequency. In as much as the correction for temperature increases as the frequency increases, it is evident also that if any accurate results are to be obtained with forks of high frequency, the question of the exact temperature of the fork and the means of keeping the temperature constant become fundamentally important. For a fork of frequency 256, the temperature correction is 0.0286 per degree Centigrade; hence an error of 0.3° C. in the temperature of the fork would account for the maximum outstanding difference in the series of values given above. Under ordinary circumstances the temperature of the fork can best be determined by attaching it to some large mass of metal, with which the thermometers may be brought into thermal contact either by means of mercury cups or by packing the bulbs in tin foil. By enclosing the fork in a hollow cylinder of metal with walls some centimeters thick it is admirably shielded from external temperature effects and its exact temperature may be very accurately determined. To the problem of rating a fork so thermally shielded the method lends itself most readily; only a single tube closed by glass plates being needed for the ingress and egress of the beam of light. The results thus far obtained seem to justify the assumption that with a fork so shielded the method will give the frequency constant in third place of decimals.

For convenience of reference a partial bibliography of the subject is appended.

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UNIVERSITY OF MICHIGAN, ANN ARBOR, March, 1901.

GEORGE FRANCIS FITZGERALD.

BY J. LARMOR.

THE eminent scientific man whose work we here propose to review was born in 1851, second son of William FitzGerald, a distinguished theologian and metaphysician, Bishop of Cork, and afterwards of Killaloe. His early education was conducted at home, in company with his brothers and sisters, under the tuition of a lady who was for many years a valued member of the household, a sister of the great mathematician and logician George Boole, who was professor in the Queen's College at Cork. He was good at all subjects requiring close observation from his earliest years. On passing to Trinity College, Dublin, at sixteen years of age, he soon made his way to the top in the classes of his year, obtaining his degree in 1871 at the head of the lists both in Mathematical and in Experimental Science. He became expert at gymnastic exercises and was for many years a fine racquet player; he also took a considerable part in the literary and social clubs of the College. His athletic skill was turned to account a few years ago in experimenting on the mechanics of flight.

The years from 1871 to 1877 were spent in reading with a view to the examination for Fellowship: vacancies were at that time very rare, but he was successful on his second time of trying. The course of study contained portions of the classical writings of Lagrange and Laplace, Hamilton and MacCullagh; and the close scrutiny of the modes of thought of masters such as these doubtless formed an admirable preparation for his subsequent scientific career. During this period he also made a formal study of metaphysics; he was much attracted by the idealism of his countryman, Bishop Berkeley, which kept cropping up in his discourses as the connecting link between material science and higher things, up to the end of his life. It formed one of the manifestations of a poetic and deeply religious temperament.

For some years after obtaining Fellowship, he served with great success as a College tutor; his side was very popular, so that it was always full a long time in advance; and his services were in great demand as a director of the social and athletic organizations of the College. He gave up tutorial work on being elected in 1881 to the Chair of Natural and Experimental Philosophy, which he retained until his death last February. The care of a laboratory not adequately endowed, and a large amount of teaching of elementary classes, took up most of his time; what remained was much broken up in acting as Examiner in Physics in other Universities, and as referee of scientific memoirs for learned Societies, in copious correspondence with scientific friends who were sure of obtaining acute and stimulating opinions on all knotty points submitted to him, and in the discharge of public duties which of late years had been increasing largely in extent and importance. Yet he found time to become one of the most learned men of the day in all branches of physical science, both theoretical and applied, and to leave his mark on the scientific progress of his age.

The physical problem attacked in his first published paper (*Roy. Soc. Proc.*, 1876) was the then recently announced Kerr effect, the displacement of the plane of polarization of light on reflection from a magnet. By an argument based on general considerations, he connects this phenomenon with the double refraction indicated by the different velocities of propagation of right- and left-handed circular vibrations in magnetized media, as Stokes and Kelvin had already independently suggested. The details of the argument are corrected in the papers next following; but by a rough numerical estimate he shows, as Kundt experimentally verified some years after, that the Faraday rotatory power in traversing a film of magnetized iron must be very great, and that the effect similar to Kerr's which must exist on reflection from a naturally rotatory substance such as quartz would be actually inappreciable. By neat and simple appliances he repeats Kerr's experiment: he moreover finds that the polarization really becomes elliptic, so that there is a phase-difference involved in addition to the rotation: in further confirmation that the effect is due to the magnetized substance and not to the field he finds that it is entirely cut off when a film of gold-leaf is spread over the reflecting pole of the magnet. At first he thought that this elliptic polarization was directly involved in the double refraction; but in the next memoir he recognized that the difference of phase must arise, like the elliptic polarization of ordinary metallic reflection, "from the efficient reflecting surface being of some depth."

The subject of the connection of light with magnetism was thus opened out, as a necessary preliminary to a more definite treatment of this problem of magnetic reflection; and, being led thereby into Maxwell's electric theory, he follows it up two years later in a memoir "On the electro-magnetic theory of the reflection and refraction of Light" (*Phil. Trans.*, 1880, pp. 691–711) presented to the Royal Society at the end of 1878, which constitutes his most complete formal treatise. Maxwell in his memoirs on electrodynamics, and particularly in the definitive exposition published in *Phil. Trans.*, 1865, had shown that the hypothesis that light consists of electric waves gives a straightforward account of the mode of its propagation in crystals, and one which is free from the difficulties attaching to the existing mechanical theories; yet he had not made any explicit application to the dynamical laws of reflection. It was left for Helmholtz to make the remark in 1870, in a footnote to his first formal memoir on the theory of electrodynamics (*Gesamm: Abhandl:* i, p. 558) that in this respect also Maxwell's theory leads directly to the observed results by supplying the appropriate boundary conditions at the transition between the official media, whereas it had proved to be impossible legitimately to adjust any definite mechanical theory so as to admit those conditions. This statement was confirmed in a detailed formal investigation published by H. A. Lorentz in 1877. The subject of reflection is not noticed by Maxwell either in the *Phil. Trans.* memoir of 1865 or in his treatise which appeared in 1873, two years after the date of Helmholtz's memoir. It seems possible, from various incidental remarks, that he was then content with the evidence afforded by the correspondence of the velocity of electric propagation in a vacuum with that of light; and that numerical discrepancies, such as that between the index of refraction in transparent bodies and the value of the square root of the specific inductive capacity, and the fact that metallic sheets are less opaque than their conductivities appeared to demand, suggested that a closer view of the vibrations of the material molecules and their interaction with the æther would have to be acquired before the dynamical problem of optical reflection became ripe for definite treatment. He was in fact in full possession as early as 1869, as Lord Rayleigh has recently shown, of the manner in which the phenomena of normal and anomalous dispersion are dominated by the influence of sympathetic vibrations in the molecules of the material medium. The analysis of this problem of optical reflection that was now independently developed by FitzGerald is of high import from the point of view of general electrodynamic theory. He first announces the proposition (most pointedly in the abstract of his memoir, *Roy. Soc. Proc.*, 1879) that by introducing a vector (ξ, η, ζ) representing the magnitude of the total disturbance of the element of æther (of whatever nature it may really be) of which the magnetic force constitutes the time-rate of growth or velocity, the electrodynamic scheme of Maxwell, for dielectric media of aeolotropic quality however general, can be immediately reduced to the standard form required by the principles of analytical dynamics; namely, the effective kinetic energy T and the potential energy W of the medium being given by the expressions[1]

$$T = \frac{\mu}{8\pi} \int (\dot{\xi}^2 + \dot{\eta}^2 + \dot{\zeta}^2)\, d\tau$$

$$W = \tfrac{1}{2} \int U d\tau,$$

where $\delta\tau$ is an element of volume and U is a quadratic function of (f, g, h) characteristic of the material medium, (f, g, h) representing the curl of (ξ, η, ζ), or

$$\left(\frac{d\zeta}{dy} - \frac{d\eta}{dz}, \frac{d\xi}{dz} - \frac{d\zeta}{dx}, \frac{d\eta}{dx} - \frac{d\xi}{dy}\right),$$

then the equations of electromotive propagation are obtained in the Lagrangian manner by annuling the variation of the action, that is from the *single relation*

$$\delta \int (T - W)\, dt = 0.$$

There are, however, other analytical expressions for T and W

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[1] In case the medium is not homogeneous μ would be inside the integral.

which would lead to the same equations of bodily propagation, as witness the various elastic mechanical theories of light which give the correct laws of transmission; in fact by integration by parts we may express $T - W$ in the form of a new volume integral together with a surface integral extended over the boundary of the region considered, and of these only the former part is concerned in the formation of equations of propagation, though the latter is essential to the relation connecting stress and strain.

FitzGerald points out, following his countryman MacCullagh, and also Green in a different connection, that not merely the equations of bodily propagation, but the equations of transition expressing continuity of stress and displacement between the media at the reflecting interface, are definitely and consistently involved in this way of formulating the problem by a single equation, the surface integrals in the reduced variation of the action determining the latter relations. He then remarks that the electric theory, as thus expressed in terms of this magnetic displacement (ξ, η, ζ), is formally identical with MacCullagh's dynamical theory of crystalline reflection and refraction published thirty years before. The problem which MacCullagh then proposed to himself was to work backward from an analysis of the actual circumstances of crystalline reflection, as determined mainly through the experiments of Brewster and Seebeck, to a type of Lagrangian functions $T - W$ for the media of propagation which would correspond in their consequences with these very various test phenomena. It has always been admitted that he was entirely successful in this analytical quest: but he definitely proclaimed his inability to conceive of any kind of material elastic medium, as ordinarily understood, whose properties would be represented by the relations finally obtained. The fact that in any material medium, in which dynamical phenomena are determined entirely by interaction between internal stress and forces of the usual non-polar kind acting from a distance, there would on MacCullagh's scheme be an unbalanced torque on each element of volume, shows that a mechanical theory of this type can subsist only if there are polar forces (*e.g.*, *quasi*-magnetic) capable of compensating the torque, or if there is a kinetic reacting torque arising from gyrostatic rotations forming a part of the constitution of the medium. In later years

Lord Kelvin showed how to construct a cellular material system with gyrostats mounted in its elements, which would form an actual model of this rotationally elastic medium of MacCullagh. The hasty assumption that the analysis of the latter must necessarily be identical with the tentative mechanical theory of F. E. Neumann, because it gave the same results, had led to the real significance of MacCullagh's investigation being overlooked at the time; doubtless too it was felt the possibilities of purely mechanical media had not been exhausted. It was accordingly an advance of prime importance when FitzGerald pointed out in 1878 that the strain, of unknown nature but known relations, which MacCullagh's theory required, was precisely the one, equally unknown to our perceptions of sense, on which Maxwell's electro-optic theory is based; his memoir in facts terminates with the remark that Maxwell's theory, if it "induced us to emancipate our minds from the thraldom of a material ether, might possibly lead to most important results in the theoretic interpretation of nature."

Other considerations may be mentioned in illustration of the significance of FitzGerald's mode of considering the subject. In the statement of electrodynamic theory elaborated by Heaviside and by Hertz, which has been widely accepted as a powerful aid to concise formulation and development, the main feature has been the elimination of the potential functions of the vector electric current and the scalar electric distribution, that were introduced in the course of Maxwell's analysis: in FitzGerald's dynamical procedure, from the basis of the principle of Least Action, no such potentials occur. Indeed Maxwell had himself pointed out (*Phil. Trans.*, 1868) that the equations of electric propagation were most compactly expressed (when their theoretical basis was not in question) by the pair of circuital relations between the fundamental vectors which result from the elimination of these potentials. In FitzGerald's analyses the relation in which the interfacial conditions stand to these bodily relations is moreover directly involved. The problem as treated by him was however limited expressly to the case of transparent media, in which there are no wandering electric charges. The natural way to extend his method to the more general questions in which charges are in finite translatory motion, either from conduction or by convection of the material system, is to retain his specification of $T-W$ for the free æther, but to introduce into the process of variation the conditions imposed by the presence of these electrons ; in the reduction of this more general problem to differential analysis suitable for material media treated as continuous, the employment of Maxwell's potentials can hardly be evaded.

The other general remark is that, in the question as to whether Maxwell's electrodynamic scheme is sufficiently wide to cover the facts, it would have been possible to reason from the optical problem of crystalline propagation already fully analyzed by Green, Neumann, and MacCullagh, in the light of the very various and easily executed optical experiments, to the more general electric problem in which crucial experiment was for a long time almost unattainably difficult. There was fair ground for the inference from MacCullagh's analysis that his scheme was the unique one of dynamical type that could lead to the laws of crystalline reflection: no demonstration of this was indeed given, but the variety of experimental laws to which the solution had to conform created a presumption almost equivalent to proof. That scheme might be made more general by assumption of effective compressibility of the medium, *i. e.*, convergence of the magnetic vector in the electric interpretation, thereby introducing compressile waves ; these would however travel by themselves in entire independence of the transverse waves. But a scheme such as Helmholtz's, which introduced to any sensible extent compressile waves interacting with the transverse ones, would in so far come into conflict with the optical evidence. This question whether Helmholtz's proposed generalization of Maxwell's theory had any actual basis remained a main problem of theoretical electrodynamics until the discovery of electric radiation by Hertz: it has now been tacitly dropped, not so much on account of any specific experiment in disproof, as through the conviction, created by the ever-widening range of correspondence between electric and optical radiations, that these are the same thing at bottom. Towards this conviction the illustrative experiments of FitzGerald and his pupils had their share in contributing. It does not appear that he ever paid much attention to the Helmholtz theory: it reposed really on ideas involving action at a distance, and from the optical point of view which we have here attempted to sketch there was no need for its wider generality.

The extension of this theory of optical reflection to the magneto-optic problem was effected by FitzGerald by introducing, after Maxwell, terms into the function $T-W$ so as to represent interaction between the imposed magnetic field and the optical vibrations in the medium. He finds, however, that the interfacial conditions in the dynamical problem could not now be satisfied by means of transverse waves alone: and, reserving the theoretical difficulty thence arising, he completes the analysis without introducing compressile waves by neglecting the condition involving the normal disturbance, as Fresnel had done under similar circumstances. This gives him a magneto-optic effect resembling in details, as regards intensity, the description published by Kerr in the same year, but without changes of phase.

Finally it is pointed out that this is only a first approximation to an exact theory, on account of the metallic character of the reflector being ignored, and of the difficulty above mentioned—the question of phase in particular awaiting a more comprehensive theory in which the relation of matter to æther would be more exactly expressed. The difficulty has since been removed by considering the effect of the imposed magnetic field to be a structural modification in the material medium, rather than a fundamental change in the dynamical relations between the electric vectors; and FitzGerald's analytical work still remains applicable. The extension of the metallic media is now formally made, as Ohm's law indicates, by taking the refractive index to be a complex quantity: with this generalization the analysis has been extended by various writers including Lorentz, Goldhammer, and Drude, but most completely by Leathem[1] and by Wind,[2] and shown to embrace satisfactorily all the mass of detail that has been brought out in recent years in experimental magneto-optic investigations.

While these developments were proceeding, FitzGerald was also taking a close interest, stimulated in part by his uncle, Dr. Johnstone Stoney, in the theory of the Crookes radiometer, then coming into shape; this he studied in its connection with the cognate subject of the constitution of the gaseous layer which supports a liquid in the spheroidal state without contact with the hot slab, and the state of stress that is as a consequence involved in it. In an elegant subsidiary investigation (March, 1888), of the state of internal pressure in a gas, arising from supposed presence of some coordination in the directions of motion of the molecules, he finds that when the directions are simply related to a single axis an internal stress of the Maxwell electrostatic type results; in the general case the stress is not specially conditioned. This result is to be expected when we reflect that it can be proved that the Maxwell type of stress is the only one, symmetrical with respect to an axis, that can maintain itself in equilibrium. In FitzGerald's point of view the normal pressure on the warm side of a vane of a radiometer may differ from that on a perpendicular cold side because the stress in the gaseous medium is not isotropic; how far this mode of representation is consistent with the more complete analysis of internal stress in gases due to temperature-gradient, by O. Reynolds and by Maxwell, has been a subject of controversy.

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[1] Phil. Trans., 1897.

[2] Archives néerlandaises, 1897; or PHYSICAL REVIEW, Vol. VI.

In 1881 a new departure was initiated in theoretical electrodynamics by J. J. Thomson, in an investigation with the aim of determining directly the effects produced by moving charged bodies, by means of Maxwell's equations of the electric field combined with the appropriate conditions at the surfaces of the moving conductors. The question is whether the hypothesis that the moving charge acts after the manner of a current-element is an independent assumption, or how far it is already implied in Maxwell's scheme of the electric field. Neglecting the self-induction of the æthereal displacement-currents surrounding a moving charged sphere, that is, assuming instantaneous transmission of effects, it was shown that the continual adjustment of the electric force in the field, so as to be normal to the conducting surface as it moved through space, entailed a magnetic field of the type demanded. Thus if the charged body carries its electric field along with it, the same as if it were at rest, that convection creates the magnetic field aforesaid. At speeds comparable with the velocity of radiation, the result of taking account of this finite velocity of the electrodynamic transmission is that the electric field thus convected, when the steady state of motion has become fully established, is somewhat flattened equatorially, and the magnetic field is correspondingly changed: but ordinary electrodynamics based on the convection of electrons can safely leave such extreme cases aside. An important result in this paper was the remark that this field of magnetic (kinetic) energy carried along by an electron involves an addition to its effective mass; the question has in fact more recently been propounded whether all inertia of matter may not be of cognate type. The paper took its rise from the magnetic deflection of the cathode stream in a vacuum tube, as described by Crookes; and, when some of the analytical computations had been corrected by Heaviside, this memoir of Thomson's constituted the beginnings of what has now become the basis of electrodynamic theory. It is interesting also to observe in it the suggestion that the nearly abrupt changes in the magnetic field arising from the sudden stoppage of the cathode particles may be responsible for the phosphorescence excited by them in the glass: how much more they are actually responsible for was revealed years after through an accidental observation of Rōntgen's. In a critical paper FitzGerald had something to add: he pointed out that as the spherical conductor of finite size, to which the analysis related, moved along, the field of æthereal displacement is suppressed in the space that the sphere comes to occupy and is instantaneously established in the space it leaves behind: these changes constitute impulsive displacement-currents: when their vector potential is added to that of the displacement-currents of the field, the result does not give the correct magnetic force—it gives in fact none at all—the current of convection of each superficial element of the charge on the sphere has to be included as well. Thomson, without explicitly including the latter, had done what comes to the same thing by addition of a term required to make the vector potential circuital, thereby implying that the æthereal current must be supplemented so as to make it everywhere circuital also. Thus on closer examination, each portion of the electric charge is found to act independently, and so far from our being able to exclude the electric charge from view by merging it in interfacial conditions, it turns out that its convection is the very cause of the phenomena of the electric field. When considered from the point of view of the æther, the hypothesis that the total current is circuital, which lies at the very root of Maxwell's theory, involves and is equivalent to the magnetic influence of moving charges, which was verified experimentally before this time by Rowland but has recently again been challenged on experimental grounds. Following out the same train of thought, FitzGerald soon after introduced order into an obscure passage in Maxwell's exposition by inserting the term representing the current due to the convection of charged bodies, which had been overlooked.

In 1882 he contributed three papers to the Royal Dublin Society on the conditions necessary to excite electric radiation; at first he was led into inconsistencies by some confusion between the true exciting cause of the radiation existing in the radiating matter alone and the displacement currents in the surrounding æther to which Maxwell formally ascribes like properties. But he gradually gained firm footing and began to think of the vector potential as something *propagated in time* from the true electric sources, yet remaining essentially the same function which Maxwell treated as an *instantaneous* potential of the true currents and the fictitious æthereal currents taken together. He concludes that the production of radiation by electrical means is possible, that "the interactions between the molecules of matter and the æther are of the same character as the electromagnetic actions with which we are acquainted," and at this early date he goes on to express the opinion that the discharge of a condenser arranged so as to have very little inductance in the discharging circuit may be made to send out actual electric radiation of manageable wave-length.

Following up this train of ideas he published towards the end of 1883 an investigation of the intensity of radiation that would be electrically obtainable. His radiator was an alternating electric current traversing a small circuit, or, as he afterwards described it, a vibrating magnetic doublet, in contrast with the later electric doublets of Hertz. In this brief, but for the time very remarkable paper, he starts with an expression for the vector potential A as *propagated* from the true current $i_0 f(t)$ in the linear circuit, namely the vector formula:

$$A = \mu i_0 \int \frac{f(t - r/c)}{r} ds;$$

then calculating the kinetic energy by the formula

$$T = \tfrac{1}{2} \int (Fu + Gv + Hw) d\tau,$$

where (u, v, w) is now total current; and $\delta\tau$ an element of volume, he finds that in the spherical shell between radii R and $R + \delta R$, this involves an amount of energy which is proportional to δR simply and another amount which also varies as R^{-2}. The latter part he identifies as belonging to the "forced displacement-currents" around the vibrator, which start the radiated displacement-currents of which the former term represents the energy. The energy thus radiated per second comes out as

$$\tfrac{8}{3} \pi^4 (i_0 A)^2 \frac{\mu}{c^3 T}.$$

where A is the area of circuit, T the period of the simple harmonic alternations of the current, and c the velocity of light. He points out that all of this formula except the numerical factor could have been obtained from the theory of dimensions alone, assuming of course the existence of clear ideas of the process involved. This radiated energy is very small in amount except for high frequencies; with 10^7 alterations of the current per second it amounts to $\frac{1}{10} (i_0 A)^2$ ergs per second. He suggests the possibility of estimating the magnetic moment of a gaseous molecule from the radiating power of the gas. He had here not quite got to the conception of identifying the source of radiation with the motions of the electrons in the molecule; Hertz afterwards approached closer when he took for his theoretical vibrator an alternating electric doublet instead of a magnetic one.

As everybody knows, the apotheosis of these studies of radiation, so clearly presented to the mental eye, came three years later in Hertz's detection of the phenomena which have now, in wireless telegraphs, become developed into a commonplace of civilization. Beyond all question the genius of Hertz deserved this success and he stands alone. But the tracing of the history of scientific thought on the eve of a great advance is always fascinating and instructive. At the very time FitzGerald was formulating these profound yet direct views, or soon after, Oliver Lodge, his close friend and in a sense his pupil, was actually engaged in feeling out the nodes of the electric waves that ran along his discharge-circuits like sound-waves along pipes, and there can be little doubt that the goal of the experimental demonstration of Maxwell's theory would have been reached along this path, though not perhaps with the same directness as Hertz attained. Indeed it appeared that phenomena of the same kind as Hertz's had been noticed long before by Joseph Henry, and had suggested thoughts of propagation of electric influences; now when we are instructed, the difficulty is so to speak to avoid them.

Referring again to this paper on the intensity of radiation, we see clearly emerging the conception of an electric source, and of the electric field as formulated in terms of vector and scalar potentials directly propagated from the sources. This is the idea which H. A. Lorentz developed into a general theory of electrodynamics in 1892, ten years afterwards. Its expression has attained to ultimate simplicity in the compact statement by Levi-Civita in 1897, that vector potential, varying as usual inversely as the distance, travels in time, with the velocity of radiation, from each element of true current, and static electric potential similarly travels from each element of electric charge, and that the electric force (on electricity at rest) and the magnetic force in the æther are expressed in terms of these potentials in Maxwell's manner. But this kind of vector potential is a difficult one for purposes of analysis of media treated as continuous, its value at a point at a distance r from a source depending on the strength of the source not at that instant but at a previous time—previous by r/c when the source is at rest. In practice Maxwell's original potentials are much more convenient: with him there is no finite propagation of potentials, their values depending on the strengths of the sources at the very instant considered, but to attain to this simplicity the change of so-called æthereal displacement must be treated as current in Maxwell's manner, as well as the convection of the charges; it is only for the total current thus constituted that the simple laws of the early electrodynamics of Ampère and Faraday are strictly applicable. In 1893 the formal development of electro-dynamic theory from this point of view, inspired at the start by Fitzgerald's electric interpretation of MacCullagh's optical analysis, and by mechanical models based on Lord Kelvin's construction for a rotationally elastic medium, and resting directly on the broad dynamical basis of the principle of Least Action, was initiated in Great Britain, and was practically complete early in 1897, running parallel in the main results, though not in method or mode of development, with Lorentz's final presentation in his tract of date 1895. This mode of investigation immediately obtained the strong and active support of FitzGerald: the discovery by Zeeman and Lorentz in 1897 of the subdivision of the lines in a spectrum by a magnetic field afterwards provided the stimulus required to attract general attention to a theory whose logical processes were difficult and unfamiliar; so that this point of view is now universally prevalent, and is perhaps occasionally pushed to extremes that would have discredited it when in the purely theoretical stage. The distinction between the analytical potentials of Maxwell and the potentials that are actually propagated from true electric sources had been, as may be gathered from the account here given, fermenting in FitzGerald's mind, though it is only recently that it has emerged into the simplicity demanded for its general recognition: it appears from one of his last letters that it had been his intention to work the subject up, if time had allowed, into a paper for the British Association last September.

FitzGerald's skill in intuitional construction was illustrated by a striking model of the functions of the æther, invented in 1885 in connection with the dynamical theory of his memoir on optical reflection. The problem was to form a simple representation of a medium possessing the rotational elasticity above described. He effected this, as regards two dimensions of space, by mounting a number of wheels freely on a board, and connecting adjacent ones in pairs in various ways by elastic bands stretched over them, so that, as the bands maintained a hold, the wheels became bound together into a single elastic system. Fixity of the centres of the wheels implied incompressibility of the medium. A rotation imparted to one of the wheels spread itself to the surrounding ones and at the same time set up elastic stress in the bands: this stress represented a field of electric or æthereal polarity—the poles being the two sides of a band, one extended the other shortened. A rotational disturbance imposed at any place in such a medium was propagated with finite speed on account of the finite moments of inertia of the wheels: the kinetic energy of the revolving wheels represented the magnetic energy of the field, which was thus a direct consequence of the changing electric strain. In the state of equilibrium free from polarization the elastic bands were supposed to be free from strain. A region in which the wheels were loose represented a conductor. An intrinsic polarity may be introduced into this medium at any place by rotating one or more of the wheels there situated, making them slip underneath the bands that pass around them: when they are released there will be a permanent field of strain, *i. e.*, an electric field. The lines of electric polarity will be circles surrounding the place, which therefore is the analogue of a free magnetic pole; an electron is not readily represented, nor therefore are electric currents which involve the transfer of charges through the medium. But we can have currents within a limited range; if the region contains perfect conductors, slip is continually taking place at their surfaces when disturbances are going on in the medium; this represents a current sheet around the surface of each conductor, which compensates the external disturbance and so avoids any penetration to the inside of the conductors. The model in fact illustrates the phenomena of dielectric propagation, which is necessarily of alternating character; but it does not include the free mobility of electric charges which is involved in an ordinary current of conduction. By employing wheels with various orientations and replacing the elastic bands by hydraulic connections, the model is capable of extension to the three dimensions of space.

The converse of this plan, which took the kinetic (*i. e.*, magnetic) energy of the medium to be rotatory, gives the rotationally elastic medium of Rankine and Kelvin, with kinetic energy translatory, which can be practically illustrated only by complicated gyrostatic systems. But here electrons can be definitely created in the medium by supernatural operations involving a kind of knotting process, while free magnetic poles cannot exist; and a true electric current being a flux of electrons, the representation is complete. Not, however entirely complete; for the nature of the mobility through the medium of the core of the electron is unspecified, though when that is postulated the model shows how its surrounding electric field necessarily travels along with the core. The nature of the core itself involves the problem of the intimate intrinsic structure of the material atom: if that were explored there would be no secrets left in nature: in electro-dynamics and optics we may, therefore, be content to know the way in which an electric field travels through the æther without ever becoming disconnected from the unknown nucleus or electron to which it belongs. The science of physics is concerned only with the interactions between the atoms, which operate through the agency of the æther in which they definitely subsist; we may attain to clear views on that subject even though we be warned off the more obscure, perhaps unfathomable, problems of the intimate nature of matter itself and of the vital manifestations of which it can become the seat.

Examination of this very interesting paper will help to elucidate the fundamental part which intuition, working by means of models and analogies, can play in the formation of physical theory. According to Helmholtz this method of procedure has been characteristic of the British School. Its advantage is that correlations between directed physical quantities, which for their mathematical expression may require intricate formal operations, are made to run parallel with actual processes with which we are conversant from experience, so that they can be considerably developed without much trouble; the transition from analogy to theory then proceeds through logical analysis of these familiar processes, in the course of which ideas become generalized and in the end but little of the original analogy may remain. Notable examples are Cavendish's modes of thought which carried him some way into the nature of electrical phenomena more than a century ago, and the ideas of Faraday which formed the foundation of his own discoveries as well as the basis of the modern point of view. An intermediate link, between bare physical intuition and fully correlated theory, has been forged in the entirely new range of dynamical thought involved in Helmholtz's cardinal discovery that permanent vortex aggregates maintain their existence (subject to the condition of stability) in a frictionless fluid medium, solely through the interaction of inertia and continuity of movement, that they in fact determine and in a sense control the entire motion of the medium to which they belong.[1] And, taking its rise from special problems of gyrostats and vortices and other steady motions, we now possess the simple and masterful generalization of the Lagrangian dynamics, foreshadowed by Kelvin and Maxwell, developed independently by Kelvin and Routh, and subsequently expounded by Helmholtz, in which the conserved momenta of permanent internal motions are considered to be a part of the constitution of the system just as much as the distribution of the masses and the geometrical configuration. So that while Lagrange and Hamilton were able to form a synthesis of the possible modes of motion of a purely dynamical system, specified as regards mass and configuration, by means of the single formula of Least Action, we are now able, as the result of a concentrated analysis, to express the laws of a dynamical phenomena that can arise in a general system more closely specified by mass and configuration and intrinsic momenta, and to lay down the limitations to which all such non-dissipative dynamical systems must conform. The question suggests itself whether, in face of so wide a synthesis, the *rôle* of analogies and models in the discovery of physical principles is not now ended: Helmholtz has in fact himself recorded that, in general physics, he found it easier to begin with wide formal relations into which the phenomena are to be fitted rather than to ascend through special analogies to more general views. Doubtless there are advances yet to come, which will arrange in still clearer and simpler order the general features of the phenomena that can arise in purely dynamical systems, and the essential limitations to which such systems are subject.

In 1882 in a paper on the electro-magnetic effects due to the motion of the Earth, FitzGerald examines the question how far Maxwell's scheme satisfies the very crucial test arising from the fact that we have here a velocity of 20 miles per second available for our observations.[1] In his treatise Maxwell had noticed, somewhat vaguely, that the general form of his electro-dynamic equations is not affected when the whole system is moving with uniform translatory velocity, if the axes of reference move along with the system and the optical consequences of this fact were doubtless present to his mind. If the æther were supposed to move along with the system this result would indeed be involved in the mere principles of relative motion. It is not true in any case for movements of rotation. In the present paper it is recognized that there would be an alteration in the force (of the second order however) acting between electric charges arising from their convection; for if they are convected alongside each other with the velocity of light their mutual attraction would disappear. But he now found from Maxwell's equations that there would be no effect produced on a moving magnet by any charges carried along with it, for there would be induced on its surface a charge which would exactly neutralize the magnetic influence of the moving external charges; and conversely there would be no force on the moving charges arising from currents or magnets which are carried along with them. In ignorance of this result, quite recently it has still been thought to be a difficulty in æther-theory, that no magnetic action of charges convected with the Earth's motion has been observed. In fact FitzGerald went about as far as possible at that early date: the complete analysis of convection involves separate treatment of the moving electricity and the stagnant æther, such as was developed first by Lorentz and then by Helmholtz and other writers ten years afterwards. Later on he was greatly interested in the discrepancy between Michelson's classical interference experiment, which suggested that the æther moved rigorously along with the earth, and the body of electric doctrine which almost demanded that it should be stagnant. He was the first to suggest the natural reconciliation, for which much theoretical evidence has since accrued—which is in fact a necessary consequence, if forces of cohesion are wholly or mainly electric—that motion through the æther affects the dimensions of solid molecular aggregations, but to an extent so minute as to be detectable only by most refined optical measurement.

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[1] For some years past FitzGerald was considerably occupied with difficult but very suggestive speculations, in part published, explaining the elasticity of the æther by a tangled structure of vortex filaments in a medium otherwise fluid.

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[1] Later he remarked the bearing of this velocity on any hypothesis that would make inertia a function of temperature; any such addition to mass would demand a large impulse in order to acquire for it the velocity of the Earth's motion.

There is a paper of this date on comets' tails. It is pointed out that Maxwell's pressure of radiation on cosmical dust, being proportional to the intensity of the radiation, is inversely as the square of the distance and so proportional to all distances to the gravitational attraction of the radiant body. For attraction thus to be changed into repulsion the mass must be very light, or its effective surface very great compared with its volume; the latter condition may be attained by external smallness of the particles. The more minute analysis that is now possible connects the repulsion directly with the reflection and absorption of the waves of radiant energy; in these processes a definite mechanical force is established whose reaction is on the surrounding æther and not on the radiant body. The validity of the principle of Least Action for the complex system æther *plus* matter implies that action and reaction are balanced for the two constituents taken together; but the pressure of radiation, now satisfactorily established on circumstantial and other evidence, shows, as Poincaré has recently admitted, that this balance cannot always be maintained for either constituent separately.

In recent years FitzGerald has taken a leading part in the critical discussions regarding the foundation of the laws of osmotic phenomena and electrolysis, and the ionization of solutions. Indeed this latter term, now universally adopted to distinguish the phenomena from ordinary dissociation, was originally due to his suggestion; last autumn, in a contribution to a British Association discussion, since abstracted *Nature*, he proposed the term electronization for the still different phenomena of molecular decomposition that are involved in the formation of the cathode streams in vacuum tubes. Some years ago he completed the work of Maxwell and Chrystal on the degree of validity of Ohm's law of conduction, by a minute test in electrolytes with powerful currents conducted through a small hole in a diaphragm; no deviation was detected, and the law possibly holds rigorously up to the point of rupture of the conducting medium.

The displacement of the lines in a spectrum towards the red, with increasing pressure of the surrounding gas, which was discovered and investigated by the Baltimore spectroscopists, he ascribed to increase of density of the surrounding matter rather than to pressure. Each molecule in the neighborhood contributes to reduce the effective elasticity of the vibrating æthereal system, in a way which when averaged up on a large scale shows itself as increase of the electric permittivity of the medium; thus the presence of the molecule must increase all the periods of free vibration: in fact Wilsing and others have observed that when the spark is taken in dense liquid media the displacement becomes large and indefinite. He has also paid much attention to the Zeeman change produced by a magnetic field, and was the first to develop in a definite quantitative manner its relation to the Faraday magneto-optic effect.

This rapid review of the acquisition and settlement of a new region in physical science has been suggested by the recent departure from amongst us of one who by general acclaim of his fellows held the position of a leader in the enterprise. It has permitted us in a way to bring to a focus our estimate of FitzGerald's powers in the domain of physical thought. Looking back from our present position of vantage on his own published work,[1] which represented but a small portion of his scientific activity, the main feature is its tentative and pioneering character and the continuous effort towards general views; we can see more in it than his contemporaries saw at the time, doubtless more even than he was clearly conscious of himself. Although an accomplished mathematician, he preferred to reason in terms of direct images of the phenomena, and to reserve algebraic representations for purposes of calculation; he had early acquired the use of the quaternion analysis, and handled it with facility, and it was interesting to watch him getting to the bottom of a tangled scheme of physical relations by jotting down a few brief vector equations. The combined efforts of many men of genius are required to take full possession of a new territory; the subject must be for a time in the air; its ideas must be refined and polished by workers with various gifts, through the mutual attrition of apparently conflicting views, before the body of doctrine emerges in a compact and intuitive form ready to take its place as common knowledge in the scientific inheritance of mankind. Here and there giants stand out, a Maxwell or a Hertz, and by some special achievement fix the attention of their contemporaries, or sometimes it may be only of their successors. But the greater number of workers are soon merged in their generation; they have helped to mould the ideas which will be the starting-point of the next, and their place may be not the less important though no definite priorities are claimed for them, or specific discoveries attached to their names.

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[1] It is expected that his scientific writings will shortly be republished in collected form.

FitzGerald has died young, in the fiftieth year of his age, before any failure or loss of freshness had come over his mental powers. Important as have been his direct contributious to the intellectual progress of his generation, his influence over his fellows has been greater still. He was the ideal gentle knight, always more ready to afford what assistance he could to others than to proceed with his own speculations; even in his lifetime he has had his reward in becoming the trusted advisor and guide of some of the foremost scientific men of the age. His brilliant discourse to the Chemical Society of London in 1896 as the Helmholtz memorial lecture is remembered there as a classic. The impression produced by his loss may be judged from the affectionate appreciations collected recently in *Nature* (March 7) from Heaviside, Lodge, Ramsay, Perry and others of his scientific contemporaries. Here it will suffice to insert some reminiscences received more recently from Lord Kelvin.

"My first meeting with FitzGerald was when we were both guests of Dr. Traill of Trinity College, Dublin, at his country house near Bushmills, Co. Antrim, in the Easter vacation of 1883 or 1884 so far as I can remember, to visit the first electric railway of the British Empire, then recently opened between Portrush and the Giants' Causeway.

"Expecting to meet a mathematician of high order, a young and distinguished Fellow of Trinity College, I found much more than the great pleasure I anticipated. Mathematics and physics in abundance and of highly interesting quality we had, but in FitzGerald's personality there was a unique combination of which I never had experience before. His enthusiasm about water-power and electricity were delightful. We had many little and some considerable troubles in reconciling steam and electric power; and whenever a linesman or a dynamo-driver (a mechanic of species then new) or a fireman or an oiler was in trouble, FitzGerald was there helping him as a comrade and acting practically as if to the manner born and educated. Our happy three days together on that occasion gave me an epitome of FitzGerald, living in an atmosphere of the highest scientific and intellectual quality, but always a comrade with every fellow-worker of however humble quality; just as I have known him ever since, and as he has been known for a quarter of a century to hosts of friends and brother workers in Ireland, England and Scotland.

"My scientific sympathy and alliance with him have greatly ripened during the last six or seven years over the undulatory theory of light and the ether theory of electricity and magnetism; and I feel keenly the scientific bereavement which his loss entailed on myself.

"As for his whole life, it seems to me that no one ever attained more nearly than FitzGerald to the chief end of man as defined by the shorter catechism of the Church of Scotland, 'to glorify God and to enjoy Him for ever.'"

NEW BOOKS.

Handbuch der Spectroscopie. Von H. Kayser. Erster Band, Hirzel, Leipzig, 1900. Pp. xxiv + 781.

This is the first volume of one of those great treatises for the preparation of which the Germans only in our day seem to have the necessary patience and industry. To gather together all that is worth recording in the subject of spectroscopy and properly arrange and classify it is in itself a formidable task. To recognize in the confused mass of the literature those things which are really of supreme importance and to give them due prominence, subordinating without ignoring the lesser communications and treating the whole in a fair yet critical spirit, is an even more difficult one. To this work Professor Kayser has given the greater part of his time for the last ten years. The thoroughness with which the matter has been taken up may be gathered from his statement in the preface. More than forty journals and sets of transactions have been looked through from the year 1860 up to the present time and all the papers dealing with spectroscopy not merely noted but read. All references to other spectroscopic work found in these papers have been looked up and the enormous collection of material thus made has been checked by comparison with the abstracts contained in the *Fortschritte der Physik*, in *Wiedemann's Beiblätter* and in the reports of the *British Association.* More than 7,000 papers have thus been brought into review and their contents rendered readily accessible to the reader by means of a carefully prepared index of authors and an entirely separate index of subjects.

In how broad a manner the author proposes in this work to deal with his subject may be inferred from the statement of the arrangement of his treatise. Five volumes are promised us. The first, which is already at hand contains the history of spectroscopy and the description and theory of apparatus; the second volume is to deal with Kirchhoff's Law and its consequences, the emission of solids, views concerning the incandescence of gases and vapors, the dependence of emission spectra upon pressure, temperature and magnetization and the classification of spectra; the third volume is to contain an account of the phenomena of absorption together with fluorescence and phosphorescence, surface color and other allied topics; in the fourth volume each element is to be taken up separately and all that is known concerning it from the spectroscopic point of view is to be gathered together; the fifth and last volume of this exhaustive manual is intended to cover the spectroscopy of the sun and stars.

The opening chapter of Vol. I. deals as already has been indicated with the history of spectroscopy. No theme perhaps were better adapted to test the qualities of a scientific writer than this. Kirchhoff and Bunsen had numerous forerunners to some of whom the great principle which they in their work definitely and finally established was more or less clearly discernible. Concerning the matter of priority in the statement of the fundamental principles of the science a great deal has been written and nearly always in a partisan spirit. To disentangle the confused meshes of this controversy and to state fairly the services to science of the various observers who prior to 1860 attacked the great problem of the relation of the bright lines of metallic spectra to the black lines discovered by Fraunhofer in the spectrum of the sun, is indeed a difficult task. Professor Kayser has performed it in a truly admirable way. No one hitherto has succeeded in presenting the facts of the case so completely or so impartially. No one has stated so clearly the claims of tho early workers in this field nor discussed more appreciatively the bearings of their discoveries upon the development of the subject. No one perhaps in considering these early contributions, many of which led up to the very threshold of the structure built by Kirchhoff and Bunsen, has been so soundly critical. No one has brought out so clearly the relations of the earlier work to that of the two investigators at Heidelberg nor has succeeded in establishing in so convincing a manner their claim as the real founders of modern spectroscopy.

The second chapter deals with the methods of producing incandescent vapors. The author considers in succession three methods: (1) The introduction of the substances to be volatilized in various flames. (2) The use of the electric arc. (3) The electric spark discharge between electrodes of the substances to be investigated on the one hand and the electric discharge through gases and vapors at small pressures on the other. Under these heads we find a very complete discussion of the properties of flame and arc and of the phenomena of the electric discharge likewise a summary of the various practical devices employed in carrying out the three methods of obtaining gas spectra.

The exhaustive manner in which these secondary question are taken up in Professor Kayser's book finds illustration in the treatment of the question of the temperature of the Bunsen flame. The sections devoted to this subject contain a detailed account of all the important attempts to determine this temperature beginning with the original computations of Bunsen and touching upon the numerous criticisms of his results offered by contemporary authors. Crova's attempt to deduce the temperature of various sources by means of the ratio of the emission of two selected wavelengths is described and finally we have a good summary of the various measurements by means of thermo-elements, beginning with Becquerel's work and concluding with the consistent determinations of Waggener und Berkenbusch. The various attempts by Becquerel, Rossetti, Crova, Abney and Festing, Lucas, Le Chatelier, Violle, and Wilson and Gray to determine the temperature of the electric arc and the measurements of the temperature of vapors in vacuum tubes under the electric discharge by De la Rive, E. Wiedemann, Naccari and Gugliemo, Warburg, Wood and Graham are discussed in an equally satisfactory manner. The numerous forms of vacuum tube applied in spectroscopy are described at considerable length and this is followed by an admirable summary of the methods employed by various investigators to secure gas spectra free from the disturbing influence of the vapors of mercury, of the hydrocarbons, of water, etc. Kayser points out that in general the vapor of mercury introduces no confusion on account of the well-established character of its spectrum and that the same is true of water vapor which gives only the well-established lines of hydrogen. Mercury and hydrogen lines indeed afford a certain advantage in that they give convenient reference points in the spectrum.

The chapter on prisms was written at the author's request by Dr. Konen. It constitutes, taken by itself, a very complete treatise on this subject and is rendered especially useful by means of a bibliography in which some 263 titles are given. The discussion is not confined to the action prisms in the visible spectrum but is extended so as to include the ultra-violet and the infra-red. The performance of rock salt, fluorite, sylvin and quartz both as regards transmitting power and dispersion are considered and the constants for these materials from the works of Schumann, Sarasin, Rubens, Paschen and others are given in tabular form. This chapter, which occupies 140 pages, is followed by an almost equally exhaustive one on the diffraction grating.

The fifth chapter of Vol. I. is entitled *Spectroscopic Apparatus*. It opens with the description of instruments for the study of the visible spectrum, beginning with the classical spectroscopes of Kirchhoff and Bunsen, and leads up in historical order to the apparatus based upon the interference methods of Michelson. The limitations of visual work are fully considered in a section devoted to the sensitiveness of the eye and this is followed by a description of the application of photography to the study of the spectrum. The treatment of photographic plates for the purposes of spectrum photography in the ultra-violet and in the infra-red is given in sufficient detail to make this portion of the volume a practical handbook. The methods by which Abney on the one hand succeeded in the photography of the infra-red and Schumann on the other extended our knowledge of the ultra-violet to wave-lengths hitherto unknown are given due prominence. The chapter closes with an account of the various methods for the study of the spectrum by means of its heating effect. The thermopile, the bolometer, the microradiometer by Boys and the radiometer of Ernest Nichols are briefly discussed and their relative merits compared. The concluding chapter of volume I. deals with the attempts to establish the wave-lengths of the chief reference lines in the spectrum in absolute measure together with the important matter of the calibration of prisms and the reduction of measurements made upon prismatic spectra to the normal scale.

If Professor Kayser succeeds in carrying his great plan to its completion, science will be indebted to him to an extraordinary degree. All those who are interested in spectroscopy will look forward eagerly to the appearance of the subsequent volumes of his great treatise.

E. L. N.

The Elements of Hydrostatics. By S. L. LONEY. Pp. 248 + xxii. Cambridge, 1900. New York, The Macmillan Co.

This little book forms an elementary treatise on the subject of hydrostatics, with special reference to its practical applications. It will recommend itself especially to students who possess a limited knowledge of mathematics, and who would find the works of Greenhill or Minchin beyond their reach. Nothing further than elementary algebra, geometry and trigonometry, and the elements of statics is presumed on the part of the reader.

The first few chapters are devoted to the discussion of the fundamental magnitudes, pressure and density. Then follow in succession chapters on the equilibrium of floating bodies, on methods of determining specific gravity, on gases, and on machines and instruments which illustrate the properties of fluids. In this chapter the hydrostatic press, the diving bell, pumps, etc., are treated. In the remaining chapters of the book such subjects are discussed as centers of pressure, rotating liquids, curves of buoyancy and tension of containing vessels.

An excellent feature of the book is its careful illustration of important principles; the demonstrations of the theorems are nearly always accompanied by illustrative examples, and followed by exercises. Numerous exercises, most of which are easy, are placed also at the ends of the chapters; the harder exercises are conveniently indicated. Most of the examples are numerical; general constants, which are apt to convey no definite meaning to beginners, are used only sparingly.

It is surprising that the subject of capillarity should be entirely neglected; it is mentioned but once in the whole book, in a single short sentence on barometer corrections. While an extended treatment of capillary phenomena would be outside of the purpose of the book, some mention might have been made of the behavior of liquid surfaces at the walls of the containing vessels. As it is, the reader, if not already acquainted with the subject, would certainly obtain the impression from the unmodified statements of the book and the figures, that the surface of a liquid under the action of gravity is horizontal throughout its entire extent.

In general it may be said that the book deserves recommendation as a clear and concise treatment of the essential principles of hydrostatics without the use of higher mathematics.

JOHN R. BENTON.

Signalling Through Space Without Wires. By OLIVER J. LODGE. Pp. 133.

There is before us an enlarged edition of "The Work of Hertz and his Successors" by Oliver J. Lodge. The first edition has already been reviewed in this journal. The present one is published under the title "Signalling Through Space Without Wires," and adds to the former edition a most useful résumé of the work done during the past few years on "wireless telegraphy." There are 72 pages in the added matter making a book of 133 pages. The new matter consists of a history of the coherer principle, the applications which Marconi and others have made of this, and of Professor Lodge's own work on syntonic telegraphy. It gives a most interesting and judicious statement of our present knowledge of this subject and well deserves a wide and thorough reading.

C. D. CHILD.

School Chemistry. By JOHN WADDELL. New York, The Macmillan Co., 1900. Pp. 278.

This book is evidently designed for a laboratory manual, supplementing the class-room work of the teacher. Starting with the study of the most common substances, the student discovers their properties, reactions and composition, and from the facts accumulated is able to understand the clear enunciation and explanation of the laws of chemistry. He then studies in detail the most important elements and compounds.

The long and varied teaching experience of the author has impressed on him the necessity of questioning the student repeatedly during the experiment and of showing clearly the relation between facts, laws and theories; his methods illustrate this.

The book does not presuppose a sufficient knowledge of physics or physical methods on the part of the student, nor are the many interrelations of the two branches considered. Until this is done, quantitative experiments in such a work are useless.

The cuts in the book are not good; otherwise it is neatly and conveniently arranged. It will certainly be well received by students and teachers of chemistry.

H. R. CARVETH.

A Treatise on Qualitative Chemical Analysis. By J. F. SELLERS. Boston, Ginn & Co., 1900. Pp. 157.

The author, realizing that the number of books on qualitative analysis is already legion, makes an extensive apology in the preface for his own. Almost every teacher can appreciate the fact that one's own method of presentation seems the best. Some useful hints are given in the chapters upon the theory and methods of analytical operations and separations. The discussion of the effect of ammonium salts and the treatment of the barium group is especially noteworthy. We should not hesitate to assign this book a place among the better class of works upon qualitative analysis.

PHILIP E. BROWNING.

A Treatise on Elementary Dynamics, dealing with relative motion mainly in two dimensions. By H. A. ROBERTS, M.A. Pp. 258 + xii. London, Macmillan & Co.

In the preface of this book the author expresses the hope "that this little treatise may be of use to candidates for mathematical scholarships, and to others whose reading is not quite elementary." The work is designed primarily for students in England, where it is customary to take a thorough course in elementary mechanics before entering upon the study of higher mathematics. A knowledge of the calculus is, therefore, not assumed on the part of the reader. In this country, where the arrangement of the curriculum is somewhat different, the book would not be so well adapted as some others to the needs of most students beginning mechanics. That it will be of use to the "others whose reading is not quite elementary," however, there can be no doubt, for it presents the subject-matter in a manner at once very scientific and very different from that of the books most used in this country.

In this book vector methods are employed almost exclusively, and the Cartesian treatment of the subject is made decidedly subordinate; while the reverse is the case in the books in most general use. The treatment is throughout clear and rigorous, and the arrangement logical.

It is possible that the contents of the book would have been better described if it had been entitled "Dynamics of a Particle," for although the dynamics of rigid bodies is not altogether neglected, less prominence is given to it than might be expected in a work on general dynamics. The rotation of rigid bodies, for example, receives no systematic treatment. A discussion of couples and their representation by means of vectors would have been very appropriate to the methods of the book; yet the author goes no further than to give the definition of a couple.

It may be said that the book is a valuable addition to the working literature of the subject, as it forms an excellent introduction to the study of vector analysis, and furnishes many elegant examples of applications of that method.

J. R. BENTON.

Album di Elettricisti Italiani ed Esteri. Milan, 1900.

A new edition of the Album of Italian and Foreign Electricians has just been issued by the Italian journal *Elettricita.* It contains 240 half-tone reproductions, chiefly from photographs, although the portraits of some of the older electricians, such as Volta, Galvani and Faraday, are from wood cuts or engravings.

This collection affords an illustration of the difficulty of securing uniformly satisfactory results by copying in half-tone a miscellaneous lot of ordinary photographic prints. There are, however, many excellent likenesses and a few strikingly good portraits.

E. L. N.

Introduction to Science. (The Temple Primers.) By ALEX. HILL. 16mo. Pp. 140. New York, The Macmillan Co., 1900.

This little volume contains the following chapters:

Definition of Science; Aim of Science; Boundaries of Science; The Relation of Philosophy to Science; The Senses the Agents of the Mind; The Extension of the Senses by Artificial Aids; Classification of the Sciences; History of Science; Method of Science; The Age of the Earth; The Ultimate Constitution of Matter; The Origin of Species; The Cause of the Coagulation of Blood; The Function of Nerve-fibers and Nerve-cells; Microphytology.

Observations Pluviometriques et Thermometriques Faites Dans Le Departement De La Gironde de Juin 1898 a Mai 1899. Note De M. G. RAYET. Pp. 73. Bordeaux, Imprimerie G. Gounouilhou. 1899. (*Received.*)

Philosophy of Voice. By CHARLES LUNN. Pp. 189. Bailliere, Tindall, and Cox, London, 1900. (*Received.*)

U. S. Department of Agriculture. Report 64. Field Operations of the Division of Soils, 1899. By MILTON WHITNEY. Pp. 198. Washington, Gov. Printing Office. 1900. (*Received.*)

Alternating Currents. An Analytical and Graphical Treatment for Students and Engineers. By FREDERICK BEDELL and ALBERT C. CREHORE, Fourth Edition, 8vo, pp. 325. Cornell Coöperative Society, Ithaca, N. Y., 1901. (*Received.*)

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THE

PHYSICAL REVIEW.

THE INFLUENCE OF TEMPERATURE UPON THE PHOTO-ELECTRIC EFFECT.

By John Zeleny.

1. The discharge of negatively electrified bodies by the impinging of light waves upon them has been studied in various phases by a large number of observers. The results obtained by these have led to the hypothesis[1] that the discharge is due to an ionization produced at the surface of the body by the rapid absorption of certain of the waves of the impinging light. There is but little known, however, as to the relative parts played in the ionization by the material of the body and by the gas occluded in it or existing as a layer upon its surface.

The study of the effects of any cause, which produces variations in the rate of the discharge, is of interest inasmuch as it may aid in leading to a more exact knowledge of the fundamental conditions necessary for the discharge itself. The changes which have been observed in the rate of the discharge by altering either the electric force between the electrodes or the distance between them or the pressure of the gas, have recently been explained by Townsend[2] as due mainly to the secondary effect of the production of new ions in the gas by the rapid passage through it of the negative ions formed by the light at the metal surface. The influence of the temperature of a body upon the rate of the discharge from its surface has not been systematically studied, although the temperature of a body no doubt has a large effect upon the amount of the gas occluded and upon the surface layer of the gas as well as upon the molecular structure of the body itself. Hoor[1] found that by heating the zinc plate used in his experiments with a Bunsen burner to 55° C., the effect of the light was much diminished. He cites this as a proof that the discharge originates in the surface layer of gas, which he thinks had been driven off at the higher temperature. Stoletow[2] states that he obtained results the opposite to those of Hoor. He placed two platinum electrodes in an air bath and by gradually heating it to above 200° C. he found that the rate of the discharge produced by the light was rather increased, although not regularly.

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[1] J. J. Thomson, The Discharge of Electricity through Gases; E. Rutherford, Proc. Camb. Phil. Soc., Vol. IX., Pt. VIII., 1898.

[2] J. S. Townsend, Phil. Mag., Feb., 1901, p. 220.

2. The present paper gives the results of some preliminary experiments on the influence of the temperature of a body upon the rate at which electricity is discharged from its surface by ultra-violet light.

In the first experiment which was tried an open cylinder made of brass wire gauze was placed upon the plate of a gold-leaf electroscope. A coil of platinum wire was supported in the center of the cylinder and connected to earth. The temperature of the platinum wire could be altered by sending an electric current through it, and the light from an arc lamp could be concentrated upon the wire by means of a quartz lens. When the electroscope and the gauze cylinder were charged positively and hence the earthed platinum wire negatively, it was found that the discharge produced by the light was two to three times as rapid while the wire was heated to about redness as when it was at room temperature.

3. The following arrangement was then adopted for studying the effect more closely. The apparatus which was used is represented diagramatically in Fig. 1, the parts, however, not being drawn to scale.

The surface from which the discharging effect of the light was observed was for the most part that of a platinum wire. Its temperature was varied by means of an electric current. A wire about 20 cms. long and having a diameter of .038 cms. was bent into the form shown at *S* in the figure (the total diameter being about 2.5 cms.). Its actual position in the apparatus is represented at *P*. The ends of the wire were soldered to the ends of the brass rods *T* and *T'*. To the same solder junctions were fastened the two copper wires *U* and *U'* which were connected to the voltmeter *V* that was used for measuring the fall of potential between the ends of the wire. The platinum wire *P* was maintained at a definite potential by means of the battery of large storage cells *B*, the negative end of which was connected to the rod *T* while the positive end was joined to earth.

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[1] M. Hoor, Beibl. z. d. Ann. d. Phys. u. Chem, p. 731, 1889.

[2] A. Stoletow, Comptes Rendus, 108, p. 1241, 1889.

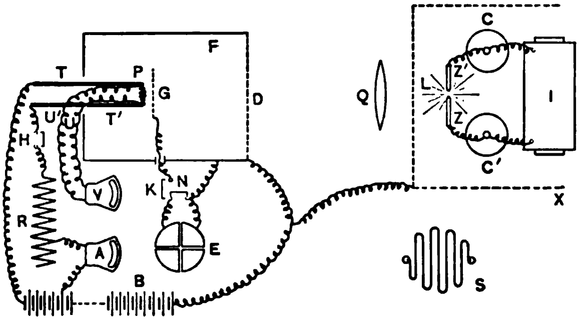

Fig. 1.

By closing the key *H*, a current from the last few cells of the battery could be passed through the wire *P*, and its amount was measured by the ammeter *A* and regulated by means of the changeable resistance *R*.

The simultaneous readings of the voltmeter *V* and the ammeter, *A* determined the resistance of the wire *P*. From this resistance the average temperature of the wire could be obtained since the resistance of the wire had previously been determined at the melting point of ice and at the boiling points of water and of sulphur. The temperature coefficient of the wire was quite low, which indicates that the platinum was not pure. The average temperature of the wire is no doubt somewhat different from the temperature of the surface of the wire with which we are concerned in these experiments. This is due partly to the uneven distribution of the temperature throughout the cross-section of the wire and partly to the cooling of the wire at the points of attachment.

The source of light used was the electric spark *L* produced between the two zinc rods *Z* and *Z'* by the induction coil *I*. A six-inch Apps coil operated by the attached hammer was used. The Leyden jars *C* and *C'* served to increase the capacity. The source of light *L* was over 50 cms. from the wire *P*, and the light was concentrated upon the latter by the quartz lens *Q* which had a diameter of 9 cms. The visible light was brought to a focus at some distance beyond *P* so that the ultra-violet light would cover but the central portion of *P*.

An insulated circular brass wire gauze *G*, having a diameter of 6 cms., was placed 1.6 cms. in front of the wire *P*. By means of the key *K* the gauze could be connected to one pair of quadrants of the electrometer *E*, the other pair of which was joined to earth. The gauze *G* could be brought to zero potential by closing both of the keys *K* and *N*.

The negative potential of *P* created the electric field between *P* and *G* under the action of which negative ions produced at *P* were carried to *G*. The rate of discharge of *P* could therefore be measured on the electrometer *E*.

The parts *P* and *G* were surrounded by an earthed metallic cage *F*, 20 cms. long and 16 cms. in diameter. The front part was made of wire gauze for the admission of the light. The electrometer with the keys and connecting wires was also covered by metallic shields not shown in the figure, the keys being manipulated from the outside by means of levers. Lastly the induction coil with the Leyden jars and spark gap were completely enclosed in a wire gauze cage connected to earth.

4. The following was the procedure in taking readings with the apparatus. The proper current was allowed to flow through the platinum wire for about a minute to allow the wire to assume a stationary temperature. Then, for temperatures below those for which the wire showed any luminosity, the zero of the electrometer was read with the key *K* closed and *N* open. The induction coil was next started by closing a key not shown in the figure, and a stop watch was started at the same time. The readings on the ammeter and voltmeter were then taken. At the expiration of a minute the induction coil was stopped, and the electrometer reading was taken after it had assumed a stationary value.

When the wire *P* was hot enough to produce a discharge owing to its temperature, the zero of the electrometer was read with both of the keys *K* and *N* closed. The coil was started, and then simultaneously the key *N* was opened and the stop watch started. The readings of the ammeter and voltmeter were then taken as before. At the end of the minute the key *K* was opened, disconnecting *G* from the electrometer, the coil was stopped and the electrometer reading taken when stationary.

A similar procedure was followed for finding the discharge due to the heated wire alone, when unaided by the ultra-violet light.

5. It was found that, while for temperatures not far from that at which the wire begins to emit light the rate of discharge was greater than that at room temperature, for some intermediate temperatures, however, the rate of discharge was less.

This is shown by the following set of readings, taken after the wire had just been used for another set of readings.

Table I.

PLATINUM WIRE.

Reference number.	Time of observation.	Resistance of wire.	Temperature.	Electrometer deflection.
1	4:10	No current.	20° C.	146
2	4:13	No current.	20	147
3	4:17	.342	80	132
4	4 20	.348	95	117
5	4:23	.390	170	91
6	4:27	.450	275	108
7	4:30	.588	520	235
8	4:33	.663	655	7*
9	4:35	.662	655	354

The platinum wire was maintained throughout at — 70.5 volts.

The reading number 8 was taken without any light on the wire and shows that at that temperature the wire was beginning to discharge negative electricity due to the heat alone. This discharge increases more rapidly with the temperature than does the discharge caused by the light, so that by increasing the temperature less than 100° above the highest used above the two become about equal. While the discharge due to the light alone can be obtained by subtracting from the total effect that caused by the heat alone, it becomes difficult to attain any high accuracy after the discharge caused by the heat becomes large, since small changes in temperature which are liable to occur affect this latter discharge greatly. This gives a limit to the temperatures that can be employed in the experiments.

The results of the above table are shown graphically in Fig. 2, where the temperatures are plotted as abscissas and the electrometer deflections as ordinates.

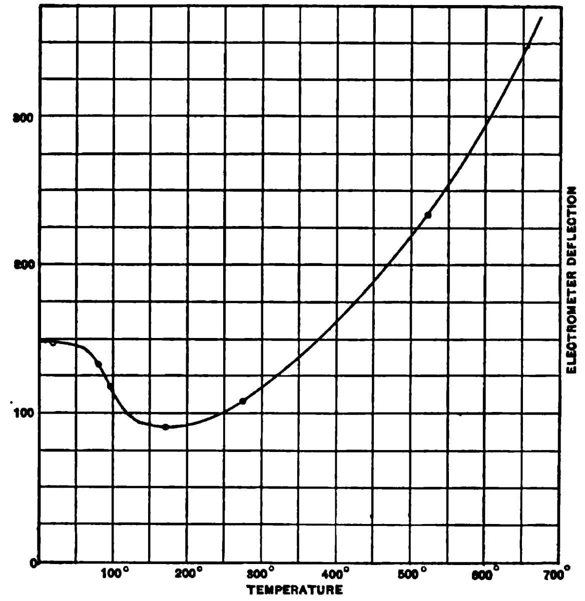

Fig. 2.

It is seen from the curve that the rate of discharge at first diminishes with increase of temperature and then finally increases. The amount of the diminution of the rate of the discharge at the minimum point of the curve, relative to the discharge at room temperature, was quite different in different sets of readings taken in the above manner. It is especially to be noted that when the wire had not been used for some time the first set of readings showed at the minimum point the smallest decrease from the readings at room temperature.

The rate of discharge at any temperature was thus found to vary for different conditions of taking the readings, depending considerably upon the immediate previous history of the wire.

The results indicate that the changes which are produced by an alteration of temperature and which affect the conductivity reach their state of equilibrium but slowly in some cases, and possibly do not attain the same stage for an increasing as for a decreasing temperature.

6. Some of these peculiarities are shown in the following set of readings where one series of observations was taken with the temperatures of the wire increasing step by step to the highest used and then diminishing similarly to room temperature; and a second series was taken like the above except that between the individual readings the wire was allowed to cool to room temperature and a reading always taken for that point.

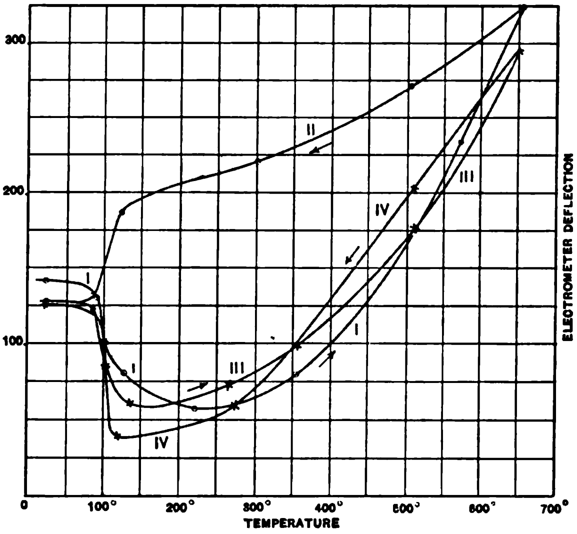

Fig. 3.

The results are shown graphically in Fig. 3.

Curve I. represents the readings for continuously increasing temperatures.

Curve II. represents the corresponding readings for decreasing temperatures.

Table II.

PLATINUM WIRE.

Reference number.	Time of observation.	Resistance of wire.	Temperature.	Electrometer deflection.
1	8 : 40	No current	20°C	140
2	8 : 43	No current	20	142
3	8 : 46	.345	90	129
4	8 : 49	.350	100	99.5
5	8 : 52	.371	125	86
6	8 : 55	.420	220	57
7	8 : 58	.492	355	80.5
8	9 : 01	.617	570	234
9	9 : 05	.664	655	8.5*
10	9 : 06	.664	655	332.5
11	9 : 09	.578	505	270
12	9 : 12.5	.464	300	221
13	9 : 16	.368	120	187.5
14	9 : 19	.343	85	130
15	9 : 22	——	20	129.5
16	9 : 25	——	20	128
17	9 : 29	.344	85	123
18	9 : 31	——	20	125
19	9 : 35	.350	100	86
20	9 : 38	——	20	122
21	9 : 41	.376	135	66
22	9 : 44	——	20	132
23	9 : 47	.445	265	72.5
24	9 : 50	——	20	106
25	9 : 53	——	20	111.5
26	9 : 55.5	.493	355	97
27	9 : 58	——	20	89
28	10 : 01	——	20	95
29	10 : 05	.581	510	177
30	10 : 08	——	20	92
31	10 : 11	.663	655	13*
32	10 : 12.5	.663	655	308
33	10 : 16	——	20	112
34	10 : 19	.581	510	203.5
35	10 : 22	——	20	107
36	10 : 25	.453	275	59
37	10 : 27	——	20	104.5
38	10 : 30	.364	115	38
39	10 : 33	.364	115	42
40	10 : 35	——	20	123.5
41	10 : 38	.350	100	101.5
42	10 : 41	——	20	126.5

Readings number 9 and 31 which are marked by a * were taken without the light, the observed discharge being produced by the heated wire alone. The potential of the platinum wire was —71 volts.

Curve III. represents the readings for increasing temperatures when the wire was cooled to room temperature after each reading.

Curve IV. represents the corresponding readings for decreasing temperatures.

The curves I., III. and IV. are practically alike except that IV. descends lower at the minimum point than the others, a peculiarity which appeared in repetitions of the observations.

Curve II. shows a larger conductivity than in the other cases, for all of the higher temperatures; as if on lowering the temperature some change produced at the higher temperature persisted through some of the lower ones.

It is noticed that at about 100° there is the most rapid change in the curves, the upper one (II.) and the lower ones approaching each other rapidly, indicating that at this temperature some more or less sudden change in the conditions takes place.

It is not possible to tell how much variation occurred in the intensity of the light during the progress of the readings, but there is reason to believe that it was not large and certainly not large enough to overshadow the peculiarities observed. The readings at room temperature at the beginning and at the end of the observations are not much different, while the two readings at the highest temperature used in the two series are also of nearly the same value. The ratio of the readings at the highest temperature to those at the temperature of the room is also the same in this series as in others which were taken at different times. Whatever disagreement exists among the readings at room temperature taken between the other readings is not necessarily all due to changes in the source of light, as there is an after effect here also which is more pronounced after a return from certain temperatures than after others.

7. The large difference between the readings at certain points for the same temperature, depending upon whether a lower or a higher temperature has been used immediately preceding is well shown by taking cycles of readings like the following:

The potential of the platinum wire was — 72 volts.

It is seen that number 4 which follows the high temperature is about three times as large as number 2, which was taken after the room temperature, although both points are for approximately the same temperature.

TABLE III.

Reference number.	Resistance of wire.	Temperature.	Electrometer deflection.
1	No current.	20° C.	92
2	.417	220	62
3	.623	590	203
4	.439	255	171
5	No current.	20	109

8. In order to find whether the effect was influenced by a change in the electric intensity between the platinum wire and the gauze, the distance between them was reduced to one third of its former value. The potential of the wire was kept the same as before, and the following set of readings was taken :

TABLE IV.

Reference number.	Resistance of wire.	Temperature.	Electrometer deflection.
1	No current.	20° C.	143
2	.419	220	64
3	.636	605	244
4	.428	240	207.5
5	No current.	20	126

Here again the large difference between numbers 2 and 4, taken after the low and high temperatures respectively, is apparent and is of about the same order as before.

9. A change in the intensity of the light was also tried, the spark being made much weaker. The following set of readings taken shows the same peculiarity with respect to numbers 2 and 4 as appears in the other cases :

TABLE V.

Reference number.	Resistance of wire.	Temperature.	Electrometer deflection.
1	No current.	20° C.	39
2	.430	240	17
3	.638	610	64
4	.426	235	43
5	No current.	20	27

10. In the above sets of readings the time interval between the successive observations was about three minutes. It was found that the conductivity observed at certain temperatures after the wire had just been cooled from some higher temperature was much larger than if the wire had not been heated. This increased conductivity is, however, in part, at least, but temporary. Some change is produced by the heating from which the wire recovers (at least partly), but in the time interval used above between the readings the recovery had not been completed, the conditions at the wire not having reached their steady state. This abnormal conductivity, therefore, gradually diminishes with time. The following set of readings illustrates this point:

TABLE VI.

Reference number.	Time of observation.	Resistance of wire.	Temperature.	Electrometer deflection.
1	9 : 22	No current.	20° C.	104
2	9 : 26.5	——	20	112
3	9 : 30	.436	250	65
4	9 : 33	.435	250	59
5	9 : 35.5	.435	250	58
6	9 : 39.5	.631	605	181
7	9 : 43	.633	605	181
8	9 : 46	.435	250	156
9	9 : 49	.434	250	138
10	9 : 53	.434	250	123
11	9 : 56	.433	245	120
12	10 : 01	.433	245	119
13	10 : 05.5	——	20	122
14	10 : 09	——	20	118.5
15	10 : 13	——	20	118.5
16	10 : 17	.434	250	62
17	10 : 20.5	.434	250	58.5
18	10 : 24	.434	250	52.5
19	10 : 27.5	.434	250	54.5
20	10 : 32	.626	590	5.5*
21	10 : 34	.626	590	167
22	10 : 36.5	.445	265	138.5
23	10 : 40	.445	265	120.5
24	10 : 43.5	.446	265	109.5
25	10 : 46.5	.446	265	102.5
26	10 : 50	——	20	106.5
27	10 : 54	.614	570	158.5
28	11 : 03	.445	265	102.5
29	11 : 06	——	20	103.5

Reading number 20 marked by a * was taken without the light. The readings from number 8 to number 12 show that after the wire had been reduced from over 600° to about 250° the conductivity at first diminished quite rapidly with time, but after fifteen minutes the change was slow, its value being then about the same as at room temperature. The readings from number 22 to number 25 also illustrate this same point. In these sets of readings the wire was exposed to the light a number of times after the heating, which fact might have been the cause of the change which produced the diminution in the conductivity. That this was not the case is shown by readings 26 to 29. Here number 28 was taken, without intermediate readings, nine minutes after number 27, and it is seen that the value of the conductivity is diminished at once to approximately the same as at room temperature.

After changing the temperature of the wire from the room temperature to about 250° the readings 3 to 5 and the readings 16 to 19 show that here also there was some diminution of the conductivity with time.

11. The preceding results show that for the range of temperatures used the conductivity produced by the impinging of the ultra-violet light upon a negatively charged platinum wire, at first diminishes with the temperature, reaches a minimum value and then increases.

After reducing the temperature of the wire to certain intermediate temperatures, the conductivity is larger at first than if such temperatures had not been exceeded shortly before; the wire acquiring its steady state but slowly in such cases. Whether the steady state is the same for a descending as for an ascending temperature is not yet determined. Careful experiments will be made on this point, for if the final state is not the same in the two cases, this must be taken as good evidence that the result is due to a changed molecular arrangement of the wire.

The recovery of the steady state after a reduction of temperature is more rapid at certain temperatures than at others.

The temperature at which, upon descending to it, the recovery begins to be especially rapid is in the neighborhood of about 100° C., at which place also the conductivity diminishes quite rapidly in the case where readings are taken when the temperatures are being increased.

12. Some experiments were performed in which the platinum wire used previously was replaced by an iron wire bent in the same form.

TABLE VII.

IRON WIRE.

Reference number.	Time of Observation.	Resistance of wire.	Electrometer deflection.
1	9 : 16	No current.	2.
2	9 : 21	.35	1.25
3	9 : 24	——	2.75
4	9 : 26.5	.35	1.75
5	9 : 30	——	2.75
6	9 : 33	.558	1.25
7	9 : 37	.558	1.
8	9 : 39	——	2.75
9	9 : 42	.714	1.25
10	9 : 46	——	1.75
11	9 : 49	.987	4.75
12	9 : 52	——	3.25
13	9 : 59	1.19	8.
14	10 : 01	——	1.5
15	10 : 04	1.30	6.
16	10 : 08	——	2.5
17	10 : 11	1.355	9.75
18	10 : 14	——	2.25
19	10 : 17	1.503	3. *
20	10 : 18	1.503	17.
21	10 : 21	——	2.
22	10 : 24	1.69	26. *
23	10 : 26	1.69	52.
24	10 : 29	——	1.75
25	10 : 33	1.875	162. *
26	10 : 36	1.875	220.
27	10 : 41	——	1.75
28	10 : 47	1.555	3.75*
29	10 : 49	1.555	13.
30	10 : 51	——	1.75
31	10 : 55	1.14	3.25
32	10 : 57	——	2.25
33	11 : 00	.403	1.
34	11 : 03	——	2.25

The conductivity obtained at the lower temperatures was very small and approached the lower limit of the electrometer.

The preceeding is a set of readings taken with the iron wire at —70 volts, the current through it being broken after every reading and the conductivity at room temperature measured. The resistance calculated from the voltmeter and ammeter readings is given in each case as before. The corresponding temperatures cannot be given because the constants of the wire were not determined. The resistance of the wire at 25° C. was .31 ohm, and when it was just beginning to glow on account of the current sent through it its resistance was about 1.30 ohms.

The readings marked by a * were taken without the light, the observed conductivity being caused by the heated wire alone.

Before reading number 13 the wire was heated more than was desired, so it was cooled to and allowed to remain at room temperature for some time. In all the readings where the resistance is not given the wire was at room temperature.

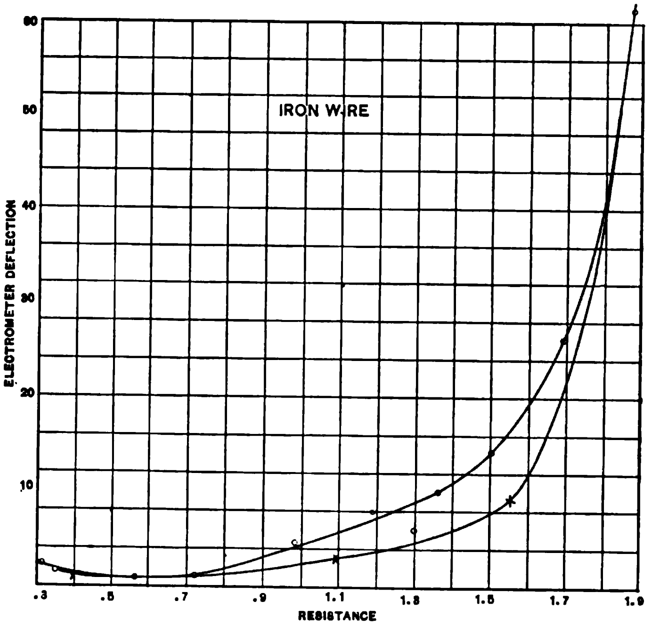

Fig. 4.

The results are shown graphically in Fig. 4, from which it is seen that as the temperature gets above what would correspond to about 700° C. the conductivity increases very rapidly. This increase with the temperature is proportionally much larger than was the case with the platinum wire. It may be worthy of notice that the large change begins in the neighborhood of the point of recalescence of the iron.

As the temperature was increased above that of the room for a considerable range the observed conductivity was diminished as was the case with the platinum wire. The smallness of the readings at these temperatures may put some doubt upon the reality of this diminution ; but a number of other readings in this same region all gave a like result. It is possible that the difference between the ascending and the descending curves is all due to variations in the light.

A set of readings taken with continuously increasing and then decreasing temperatures, as was done in the case of the platinum, did not show the same tendency for the readings taken when the temperatures were decreasing, to exceed those taken for the same points when the temperatures were increasing.

13. The photo-electric effect presents the peculiarity that negative charges alone are dissipated by the light. It may be, from the very nature of the action, that only negative charges can be affected ; but it is possible that the existing forces simply hinder the removal of the positive charges more than of the negative and that in the former case the action of the ultra-violet light cannot overcome them.

Now when a body is heated it acquires at a certain temperature the power to discharge positive electricity from its surface, and at a somewhat higher temperature it discharges the negative also. It seemed possible therefore that, especially if the nature of the process of ionization due to the heat is at all analogous to that in the discharge by ultra-violet light, the resistance to the removal of the positive charge by the light might be sufficiently weakened at the higher temperatures to enable the light to overcome it.

Under such conditions if the wire were heated to a temperature where it was almost on the point of discharging positive electricity without any light, the addition of the influence of the latter ought to produce a discharge ; while on the other hand if the wire were sufficiently hot to produce a discharge of the positive, the addition of the light ought to increase this discharge.

The experiment was tried both with a platinum and an iron wire in the apparatus, charged in each case to +75 volts and maintained at a temperature not quite sufficient to discharge positive electricity. When the light was turned on, no certain leakage could be detected and if present at all it was certainly less than one division per minute.

When the platinum wire was heated to a dull red so that it discharged positive electricity slowly, the following readings were taken without the light and with the light, the action being allowed to continue for three minutes in each case.

TABLE VIII.

PLATINUM WIRE. POSITIVE.

Time in minutes.	Electrometer deflection.	
	Without Light.	With Light.
1	14.	14.5
2	27.	26.5
3	39.5	39.5

An iron wire heated similarly gave the following readings per minute, the light being on and off alternately in this case.

TABLE IX.

IRON WIRE. POSITIVE.

Light.	Electrometer deflection.
On.	102.5
Off.	101.
On.	101.5
Off.	101.
On.	101.

The results indicate that within the limits of the experiments the action of the light was without appreciable effect.

The process of the ionization in the discharge due to the heat must be quite different from what it is in the case of the light discharge. Such mechanical movements as may be produced by the absorption of the light do not appreciably affect the discharge of the positive electricity which is caused by the heat. Whether such movements have any influence upon the discharge of the negative electricity by the heat is not certain from the experiments performed.

The following simple view may be taken of the cause of the unipolarity of the discharge produced by ultra-violet light.

The absorption of the light waves gives rise to intra-molecular forces which tend to separate a small negatively charged corpuscle[1] from the rest of the neutral molecule. The maximum impulse so given to the negative particle may give it a velocity away from the surface sufficient to carry it beyond what is called the range of molecular action, while the same outward impulse acting upon the much larger positive mass is not sufficient to get it beyond the influence of the attracting forces. We must consider the attraction tending to bring the departing particle back to the surface as not alone an electrical one or due altogether to the part of the molecule from which it has been separated, but as arising also from the attraction of all of the molecules within the range of molecular action. This latter force pulling the particle back to the surface is proportional to its mass and is therefore much the larger for the positive particles. Since the maximum outward impulses, in some way due to the light, are the same when given to a negative particle as when given to a positive one, it is possible to see how the light is effective in discharging the negatively electrified bodies alone.

When an unelectrified body is exposed to the light some of the negative ions being projected from the surface by the light action, diffuse away leaving the body charged positively. The electric field which is thus produced finally puts a stop to the increase of the charge by preventing further diffusion. By blowing past the surface the ions are carried away mechanically in opposition to the electrical forces and so the body may be charged to a higher potential.

To account for the lack of aid given by the light to the discharge of a positively electrified glowing wire we must consider any impulse given to the positive ion by the action of the light as too small to be noticed. This is quite plausible, since, according to the results of J. J. Thomson (loc. cit.), the mass of the negative particle which the light is just able to force away is only about one thousandth part of the mass of a hydrogen atom.

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[1] The existence of such corpuscles is evidenced by the researches of J. J. Thomson. Phil. Mag., December, 1899.

14. The experiments here described were interrupted nearly a year ago by derangements caused by the removal of our laboratory to temporary quarters. As there must still be some delay in resuming the work it was thought best to publish this account at this time.

As soon as possible, however, the work will be continued and it is intended to study carefully the effect of temperature changes upon the discharge from different metals when surrounded by different gases at different pressures. It is also desirable to carry the experiments to higher temperatures. At least two methods suggest themselves.

As stated before the difficulty lies in the presence of the larger conductivity caused by the glowing wire.

Now the results of Rutherford [1] and McClelland [2] show that the ions in the case of discharge by ultra-violet light travel with a greater velocity in the same electric field than those given off by the glowing wire. It would therefore be possible by blowing a properly regulated stream of gas across the path of the ions, to prevent the slower moving ions formed by the glowing wire from reaching the positive electrode, while some of those caused by the ultra-violet light would still get to it. The ions due to the heated wire being thus blown away, it would be possible to make measurements on the changing quantity of those caused by the light.

Probably a better method would be a modification of one devised by Rutherford (loc. cit.) for measuring the velocity of the ions. An alternating electromotive force is used between the two electrodes so that the direction of motion of the ions is periodically reversed. The electric intensity could be so regulated that the slower moving ions due to the heat in making their excursions from the glowing wire would not reach the other electrode, while the negative ions due to the ultra-violet light would reach it, before the reversal of the electromotive force occurred. Here again an electrometer joined to the latter electrode would show effects due alone to the ions produced by the action of the light.

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[1] Rutherford, Proc. Camb. Phil. Soc., Vol. IX., Pt. VIII., p. 401.

[2] J. A. McClelland, Phil. Mag., July, 1898.

15. The results of the experiments described above show that temperature has a large influence upon the photo-electric effect. From a platinum wire the negative electricity is at first discharged more slowly as the temperature is increased; the rate of discharge reaches a minimum, however, and then increases as far as the highest temperature used (about 700° C.).

The rate of the discharge produced by the light also depends upon the immediate previous history of the wire. On coming to certain temperatures from a higher one the rate of discharge is much greater than if a lower temperature had been used just before. For small ranges at least this effect appears to be independent of the electric intensity and of the intensity of the light. After the reduction of temperature the rate of discharge gradually becomes smaller with time, showing that the large conductivity at first is due partly at least to the fact that the wire reaches its steady state but slowly. The recovery is much faster at temperatures below a certain point than for those above, the change being fairly abrupt.

From an iron wire the rate of discharge also appears to diminish at first with the temperature but after reaching a minimum it finally becomes a great many times its value at room temperature.

Heating the wire does not change the inactivity of the light for discharging positive electricity, even though the wire is raised to a temperature where, due to the heat alone, the positive electricity is being discharged.

The fact that after the platinum wire has had its temperature reduced the larger conductivity of the higher temperature persists for a time, there being a gradual recovery, shows that at least most of the variations which have been noticed in the experiments described are due to changes taking place at the metal surface and not in the gas between the electrodes. The comparatively abrupt change in this effect occurring at about 100°C. may indicate some molecular alteration of the metal. Any further discussion had best be delayed until the completion of further experiments.

University of Minnesota, April, 1901.

CURRENTS AND POTENTIALS ON SUBMARINE CABLES PRODUCED BY SINE-WAVE ELECTROMOTIVE FORCES.

BY A. C. CREHORE.

THE problem of the transmission of current and potential in submarine cables has received the attention of the most able physicists, and its solution in a very general form is well established. Fourier gave mathematical solutions in several different forms of the differential equations involved, and these have been applied to the physical problem of the transmission of electrical energy along wires.

While these general solutions are most important as they reveal the nature of the problem suggesting certain relations and laws, which are otherwise not obtainable, yet there is something unsatisfactory about them unless some application is made to a particular case of existing or possible physical conditions, for the actual physical constants involved may give unexpected prominence to certain terms of the general solution, or the physical conditions may be such as to render the solution imaginary.

At the present time there are few examples obtainable of curves of current and potential calculated for particular submarine cables. The case which Lord Kelvin has published with the well-known curves of current and potential, applies only where a battery or constant source of electromotive force is employed. Since condensers are almost universally employed at each end of a cable, the case of the application of a constant potential to the cable itself is not one which exists in practice. With either a battery or a sine-wave transmitter the potential at the transmitting end of the cable itself does not remain constant through a single signal. With a battery transmitter the potential on the cable rises suddenly (almost instantaneously) at the beginning of the signal to approximately the full battery pressure, and gradually decreases from that point by an exponential curve as the condensers become charged until the cable is connected to earth at the end of the signal. With a sine-wave transmitter the change of potential is less sudden, and the curve of variation follows an entirely different law.

In view of the difficulty attending the exact solution of this problem for an actual case of duplex working, a method of obtaining an approximate solution which gives results not very far from the truth, when a sine-wave form of electromotive force is used in transmission, is given and curves calculated for an existing trans-Atlantic cable. The method only applies to the transmitting end of the cable. The receiving end is perhaps the more important, for the signals must be received in legible shape, if the transmitter has any commercial value; but the transmitting end is also important for it is there that the cable experiences the greatest potentials, and the insulating material the greatest strain. It is important to accomplish the best results at the receiving end by that method which subjects the transmitting end of the cable to the least electrical strain. In a cable the pressure is rapidly reduced in proceeding from the transmitting end, being in the particular Atlantic cable referred to, one-half its value at about 175 knots, the total length of the cable being 2,164 knots.

It has been shown[1] that the measurements of alternating currents and potentials at the transmitting end of the cable referred to are in agreement with the accepted theory within the limits of error of the measurements. No mention is there made, however, of the changes which take place when the electromotive force is first introduced, before the alternating current has attained its final value, and it is the present purpose to study these changes as well as the forms when rectified pulses, consisting of semi-sinuses in the same direction, are employed as in sending certain cable signals.

The curves have more value, however, than would be the case if they were merely approximate solutions for the cable circuits, for they are the exact solutions of the phenomena taking place in a real circuit, which is taken to be the approximate equivalent of the cable circuits.

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[1] "A Practical Transmitter Using the Sine-wave for Cable Telegraphy, etc." Trans. A. I. E. E., May, 1900.

The arrangement of the cable circuits is shown in Fig. 1, where the cable terminal is represented at C and the artificial cable at C′. The branches from the apex A to C and C′ contain the bridge condensers. The branch AE from apex to earth contains the armature of the alternating current generator.

The data of the circuits is as follows :

Cable :—No. 3, Atlantic cable of the Commercial Cable Co., from Canso, Nova Scotia, to Waterville, Ireland.

Length,	2,164 knots.
Resistance,	4,895 ohms.
Capacity,	914 microfarads.
Duplex bridge condensers,	80 microfarads each.
Armature resistance,	59 ohms.
Armature inductance,	3.555 henrys.

The equivalent circuit is one in which the same harmonic electromotive force produces the same harmonic current both in magnitude and phase relation to the electromotive force. If the circuits of Fig. 1 from the point A, including both the real and artificial cables and the condensers, are replaced by a simple circuit having resistance and capacity, as in Fig. 2, the values of the condenser and resistance may be so proportioned that neither the harmonic current through the armature, nor the phase relation to the electromotive force will be altered.

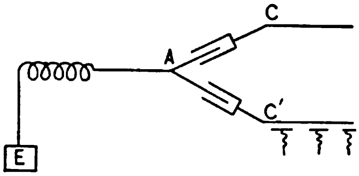

Fig. 1.

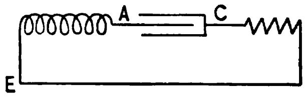

Fig. 2.

Since it has been shown that the apparent impedance of the cable differs according to the frequency, the following calculations have been based upon a frequency of $n = 5$. This represents a speed of cable working of 162 letters per minute.

Data of equivalent circuit for frequency $n = 5$.

$$R = 146.255 \text{ ohms.}$$
$$C = 92.208 \text{ microfarads.}$$

Including the resistance and inductance of the armature the data for the whole circuit (Fig. 2) is:

$$R = 205.255 \text{ ohms.}$$
$$L = 3.555 \text{ henrys.}$$
$$C = 92.208 \text{ microfarads.}$$

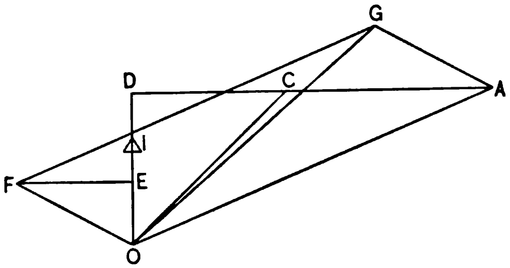

Fig. 3.

All numbers represent maximum harmonic values.

OC = 42.426 volts; assumed cable potential between C and E, Fig. 1.
OD = 30 volts; component of cable pressure in phase with the current.
DC = 30 volts; component of cable pressure in quadrature with the current.
COD = 45°, or $\pi/4$ radians.
OI = .2051 ampère; current in the apex A, Fig. 1, equal to twice the cable current and in phase with it.
CA = 40.807 volts; pressure across the bridge condenser, 80 microfarads in branch AC, Fig. 1.
OA = 76.902 volts upon apex between A and E, Fig. 1.
OE = 12.102 volts; drop through armature resistance.
EF = 22.909 volts; drop through armature inductance.
OG = 63.773 volts; generated by the alternator.
DOG = 48° 41′ 10″ or = .8497 radians = θ.

When an harmonic current is flowing in the circuits, Fig. 1, the diagram, Fig. 3, represents the harmonic currents and potentials for the case where the potential on the cable is assumed to be 30 virtual, or 42.426 maximum, volts. The volts required from the generator to produce this upon the cable are, OG, 63.773 (max.) and this produces a maximum of 76.902 upon the apex A. The current in the generator has a maximum value of .2051 ampère and is in advance of the generated electromotive force OG, by an angle of 48° 41′ 10″. The angle between the apex electromotive force and the current AOD is 67° 2′ 20″.

The diagram, Fig. 3, gives the state of electromotive forces when the stable condition is attained. The approximate potentials when the electromotive force is introduced into the circuit will be found by calculating the current which the electromotive force would produce in the equivalent circuit, and assuming that the current in the armature will be approximately the same with the cable circuit. Figs. 4–9 inclusive apply only to the equivalent circuit, and 10 and 11 apply to the cable circuit, Fig. 1. The quantities may be easily calculated for the equivalent circuit. The equation of the impressed electromotive force is

$$(1) \qquad e = E \sin \omega t.$$

The differential equation applying to the circuit is:

$$(2) \qquad L\frac{d^2q}{dt^2} + R\frac{dq}{dt} + \frac{q}{C} = E \sin \omega t.$$

where q is the charge in the condenser.

The solution of this equation is written in three forms as R^2C is greater than, equal to, or less than $4L$. In the case under consideration $4L$ is greater than R^2C, the circuit being oscillatory, and the solution is:

$$(3) \qquad q = -\frac{I}{\omega}\cos(\omega t + \theta) + A\varepsilon^{-\frac{Rt}{2L}}\sin(at + \varphi),$$

where,

$$I = \frac{E}{\sqrt{R^2 + \left(\frac{1}{C\omega} - L\omega\right)^2}} \quad \text{and,} \quad \theta = \text{arc tan}\left(\frac{1}{CR\omega} - \frac{L\omega}{R}\right),$$

$$a = \frac{\sqrt{4LC - R^2C^2}}{2LC} \quad \text{and,} \quad \delta = \text{arc tan} -\frac{2La}{R}.$$

A and φ are the arbitrary constants determined by the initial conditions assumed.

For the curves shown it is assumed that the electromotive force is introduced at its zero phase, that is when it has zero value when changing from negative to positive, and that the charge and current in the circuit at the time of introducing the electromotive force are q_n and i_n respectively. The equation of the current obtained by differentiating (3) is:

$$(4)\qquad i = I\sin(\omega t + \theta) + \frac{A}{\sqrt{LC}}\varepsilon^{-\frac{Rt}{2L}}\sin(at + \varphi + \delta).$$

When $t = 0$, we have $q = q_n$, and $i = i_n$. Hence, from (3),

$$(5)\qquad q_n = -\frac{I}{\omega}\cos\theta + A_n\sin\varphi_n,$$

from (4),

$$(6)\qquad i_n = +I\sin\theta + \frac{A_n}{\sqrt{LC}}\sin(\varphi_n + \delta).$$

Solving for φ_n we have,

$$(7)\qquad \cot\varphi_n = \frac{i_n - I\sin\theta}{\left(q_n - \frac{I}{\omega}\cos\theta\right)a} - \cot\delta.$$

The value of A may be found by substituting (7) in (5) or (6). In calculating numerical values care must be taken to employ the correct value of the angle δ. The tangent of this angle has been given as negative, but this will permit of two angles, in the second or the fourth quadrant. From a consideration of the differential equation[1] (2) it will appear that in order to satisfy the equation, $\cos\delta$ is negative, which determines that δ is an angle in the second quadrant.

The numerical values of the constants for the case assumed are:

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[1]
$$L\frac{d^2q}{dt^2} = L\omega I\cos(\omega t + \theta) + \frac{A}{C}\varepsilon^{-\frac{Rt}{2L}}\sin(at + \phi + 2\delta)$$

$$R\frac{dq}{dt} = RI\sin(\omega t + \theta) + \frac{RA}{\sqrt{LC}}\varepsilon^{-\frac{Rt}{2L}}\sin(at + \phi + \delta)$$

$$\frac{q}{C} = -\frac{I}{C\omega}\cos(\omega t + \theta) + \frac{A}{C}\varepsilon^{-\frac{Rt}{2L}}\sin(at + \phi)$$

By addition

$$e = E\sin\omega t = I\sqrt{R^2 + \left(\frac{1}{C\omega} - L\omega\right)^2}\sin\omega t + A\varepsilon^{-\frac{Rt}{2L}}\left\{\frac{1}{C}\sin(at + \varphi + 2\delta) + \frac{R}{\sqrt{LC}}\sin(at + \phi + \delta) + \frac{1}{C}\sin(at + \phi)\right\}.$$

Hence

$$\frac{1}{C}\sin(at + \phi + 2\delta) + \frac{R}{\sqrt{LC}}\sin(at + \phi + \delta) + \frac{1}{C}\sin(at + \phi) = 0.$$

Hence

$$\cos\delta = -\frac{RC}{2\sqrt{LC}}.$$

$$a = 47.088.$$
$$\delta = 121^\circ\ 30'\ 40'' = 2.1208 \text{ radians}.$$
$$R/2L = 28.868.$$
$$T = .1336 \text{ second} = \text{period of circuit}.$$

A description of the curves giving the numerical equations in each case is added. It is to be noticed in general that the potential in no case rises higher during the initial stages than the value which it attains when it has reached the steady state, and it thus appears to be a safe rule to find the maximum potentials by the simple calculation of the maximum values when an harmonic condition is reached.

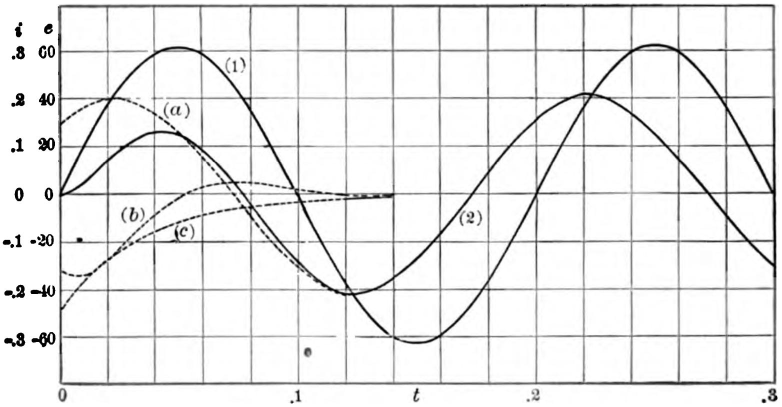

Fig. 4.

Curve (1). Impressed electromotive force, alternating, harmonic, introduced at zero phase, initial charge and current being zero.

$$e = E \sin \omega t.$$
$$e = 63.773 \sin 31.416\, t.$$

Curve (2). Resulting current in equivalent circuit, Fig. 2.

curve (2) = curve (a) + curve (b).

(a) $$i_a = I \sin (\omega t + \theta).$$
$$i_a = .2051 \sin (31.416t + .8497).$$

(b) $$i_b = \frac{A}{\sqrt{LC}} \varepsilon^{-\frac{Rt}{2L}} \sin (at + \phi + \delta).$$

$$i_b = -.2406\, \varepsilon^{-28.87t} \sin (47.088t + .6949).$$

(c) $$i_c = -.2406\, \varepsilon^{-28.87t}.$$

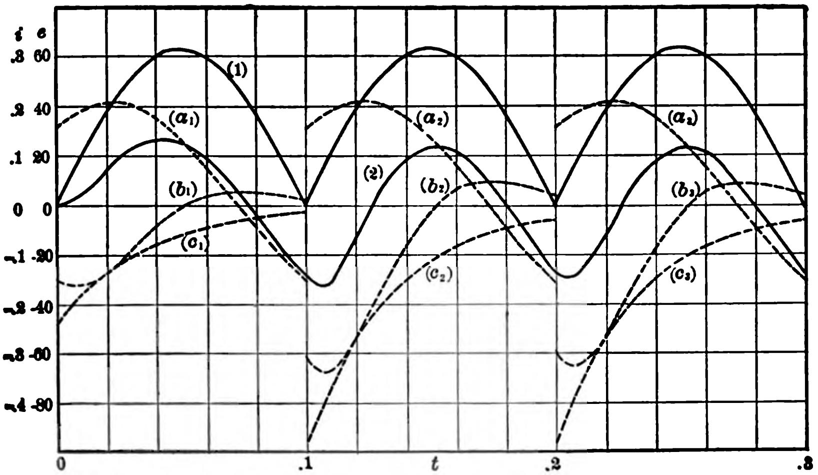

Fig. 5.

Curve (1). Impressed electromotive force, pulsating harmonic, introduced at zero phase, initial charge and current being zero at beginning of first semi-cycle.

Equation the same as for Curve (1), Fig. 4, the origin being transferred to points $t = .1$, $t = .2$, $\cdots$, $t = \frac{n-1}{10}$ for the second, third and nth semi-cycles.

Curve (2). Resulting current in equivalent circuit, Fig. 2.

Curve (2) = curve (a) + curve (b).

(a_1) Same as (a), Fig. 4, (first semi-cycle). Equation of (a_2) (a_3), $\cdots$, (a_n) for second, third and succeeding semi-cycles same as (a), Fig. 4, with origin transferred to points $t = .1$, $t = .2$, $\cdots$, $t = \frac{n-1}{10}$ respectively.

(b_1) Same as (b), Fig. 4 (first semi-cycle).

(b_2) $$i_{b_2} = \frac{A_2}{\sqrt{LC}} \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi_2 + \delta).$$

$$i_{b_2} = -.4813\,\varepsilon^{-28.87t} \sin(47.088t + .6669).$$

(b_3) $$i_{b_3} = \frac{A_3}{\sqrt{LC}} \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi_3 + \delta).$$

$$i_{b_3} = -.4811\,\varepsilon^{-28.87t} \sin(47.088t + .6393).$$

(c_1) Same as (c), Fig. 4.

(c_2) $i_{c_2} = -.4813\,\varepsilon^{-28.87t}$.

(c_3) $i_{c_3} = -.4811\,\varepsilon^{-28.87t}$.

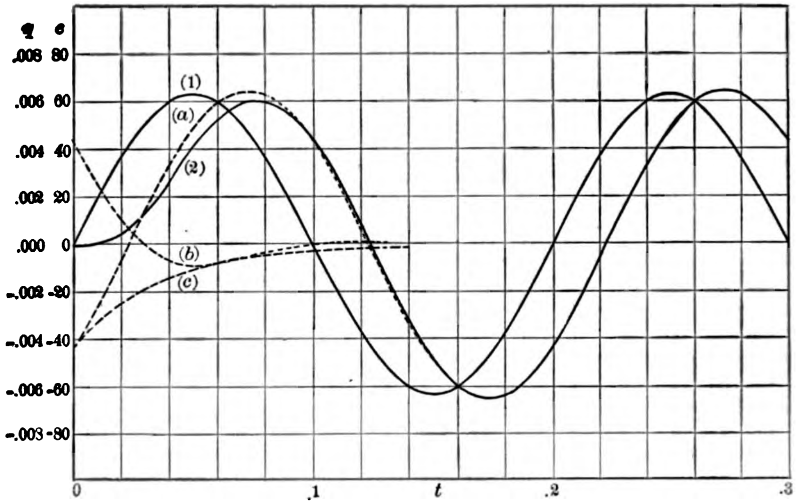

Fig. 6.

Curve (1). Impressed electromotive force alternating. Same as (1), Fig. 4.

Curve (2). Resulting charge in the condenser of circuit, Fig. 2.

Curve (2) = curve (*a*) + curve (*b*).

(*a*) $$q_a = -\frac{I}{\omega}\cos(\omega t + \theta).$$

$$q_a = -.006529\cos(31.416t + .8497).$$

(*b*) $$q_b = A\epsilon^{-\frac{Rt}{2L}}\sin(at + \phi).$$

$$q_b = -.004356\epsilon^{-28.87t}\sin(47.088t - 1.426).$$

(*c*) $$q_c = -.004356\epsilon^{-28.87t}.$$

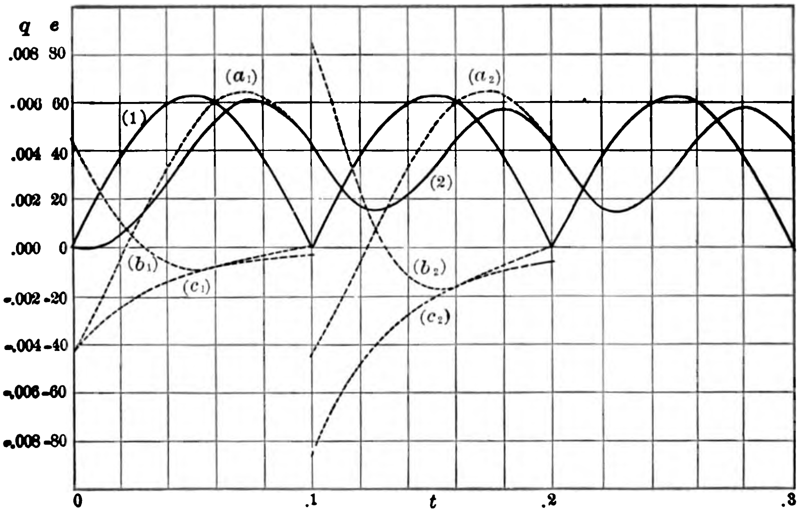

Fig. 7.

Curve (1). Impressed electromotive force pulsating. Same as (1), Fig. 5.

Curve (2). Resulting charge of the condenser.

Curve (2) = curve (a) + curve (b)

(a_1) Same as (a), Fig. 6 (first semi-cycle). Equation of (a_2), (a_3), ..., (a_n) for second, third and succeeding semi-cycles are the same as (a), Fig. 6, with the origin transferred to points $t = .1$, $t = .2$, ..., $t = \frac{n-1}{10}$.

(b_1) Same as (b), Fig. 6.

(b_2) $q_{b_2} = A_2 \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi_2)$.

$q_{b_2} = -.008714 \varepsilon^{-28.87t} \sin(47.088t - 1.4539)$.

(b_3) $q_{b_3} = A_3 \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi_3)$.

$q_{b_3} = -.008710 \varepsilon^{-28.87t} \sin(47.088t - 1.4815)$.

(c_1) Same as (c) Fig. 6.

(c_2) $q_{c_2} = -.008714 \varepsilon^{-28.87t}$.

(c_3) $q_{c_3} = -.008710 \varepsilon^{-28.87t}$.

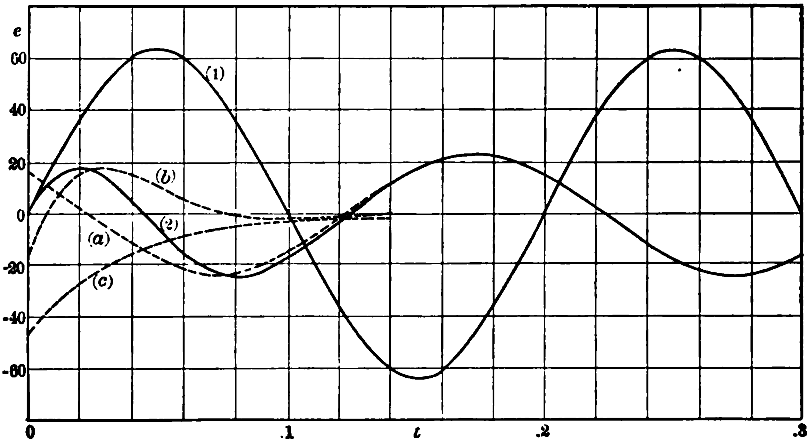

Fig. 8.

Curve (1). Impressed electromotive force alternating. Same as (1), Fig. 4.

Curve (2). Resulting electromotive force required to overcome the inductance of the armature in circuit, equal to $L \frac{d^2q}{dt^2}$.

Curve (2) = curve (a) + curve (b).

(a) $\left(L \frac{d^2q}{dt^2} \right)_a = L\omega I \cos(\omega t + \theta)$.

" $= 22.909 \cos(31.416t + .8497)$.

(b) $\left(L \frac{d^2q}{dt^2} \right)_b = \frac{A}{C} \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi + 2\delta)$.

" $= -47.24 \varepsilon^{-28.87t} \sin(47.088t + 2.8157)$.

(c) $\left(L \frac{d^2q}{dt^2} \right)_c = -47.24 \varepsilon^{-28.87t}$.

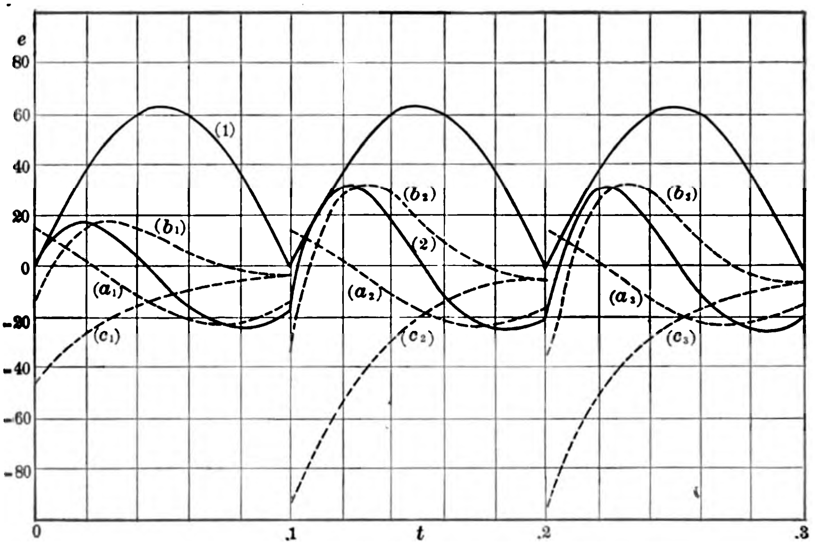

Fig. 9.

Curve (1). Impressed electromotive force, pulsating. Same as (1), Fig. 5.

Curve (2). Resulting electromotive force to overcome the inductance of the armature, equal to $L\dfrac{d^2q}{dt^2}$.

$$\text{Curve } (2) = \text{curve } (a) + \text{curve } (b).$$

The equations of (a_1), (a_2), ..., (a_n) for the first, second and following semi-cycles are the same as (a), Fig. 8, with the origin at the points $t = 0$, $t = .1$, ..., $t = \dfrac{n-1}{10}$ respectively.

(b_1) Same as (b), Fig. 8. (First semi-cycle.)

(b_2) $$\left(L\frac{d^2q}{dt^2}\right)_{b_2} = \frac{A_2}{C}\,\varepsilon^{-\frac{Rt}{2L}}\sin(at + \phi_2 + 2\delta).$$

$$\text{“} \quad = -94.504\varepsilon^{-28.87t}\sin(47.088t + 2.7877).$$

(b_3) $$\left(L\frac{d^2q}{dt^2}\right)_{b_3} = \frac{A_3}{C}\,\varepsilon^{-\frac{Rt}{2L}}\sin(at + \phi_3 + 2\delta).$$

$$\text{“} \quad = -94.460\varepsilon^{-28.87t}\sin(47.088t + 2.760).$$

(c_1) Same as (c), Fig. 8.

(c_2) $$\left(L\frac{d^2q}{dt^2}\right)_{c_2} = -94.504\varepsilon^{-28.87t}.$$

(c_3) $$\left(L\frac{d^2q}{dt^2}\right)_{c_3} = -94.460\varepsilon^{-28.87t}.$$

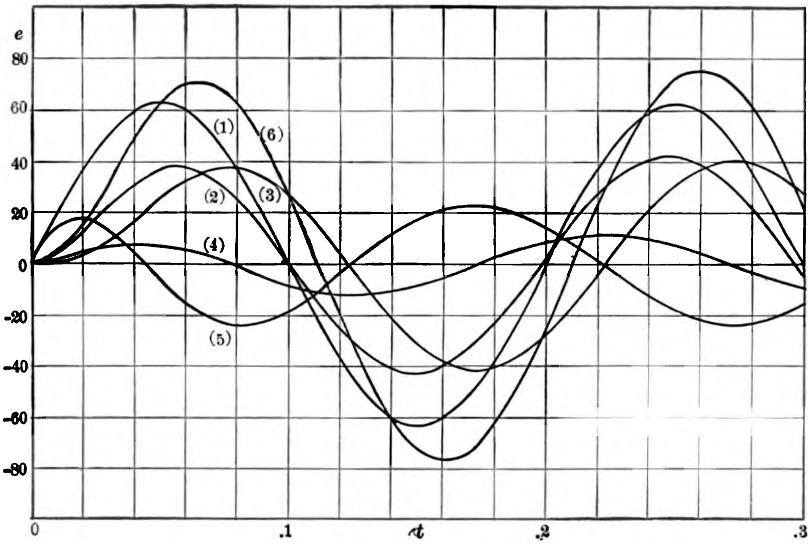

Fig. 10.

Curves of electromotive forces in the duplex cable circuits (Fig. 1), assuming that the current in the apex *A* is the same as that in the equivalent circuit (Fig. 2).

Curve (1). Harmonic alternating electromotive force generated by the alternator, and required to drive the current, curve (2), Fig. 4, into the apex of the cable. Same as curve (1), Fig. 4.

Curve (2). Resulting potential difference between the cable C and the earth E, Fig. 1.

Curve (2) = curve (1) — curve (3) — curve (4) — curve (5).

The cable potential curve (2) is found graphically by subtracting from the impressed electromotive force (1) the electromotive to overcome the resistance of the armature (4), the inductance of the armature (5) and the bridge condenser (3).

Curve (3). Potential drop across the bridge condenser AC, Fig. 1; $V = \frac{q}{C}$. One bridge condenser receives one-half the current and charge in the apex circuit.

Since the capacity of the bridge condenser is 80 microfarads, the equation of curve (3) is

$$\frac{q \times 10^6}{160} = -\frac{I \times 10^6}{160\omega} \cos(\omega t + \theta) + \frac{A \times 10^6}{160} \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi).$$

$$= -40.808 \cos(31.416t + .8497) - 27.224\varepsilon^{-28.87t} \sin(47.088t - 1.426).$$

Curve (4). Potential drop due to resistance of armature, equal to *Ri*, or 59*i*. Hence

$$59i = 59I \sin(\omega t + \theta) + \frac{59A}{\sqrt{LC}} \varepsilon^{-\frac{Rt}{2L}} \sin(at + \phi + \delta).$$

$$59i = 12\,102 \sin(31.416t + .8497) - 14.195\varepsilon^{-28.87t} \sin(47.088t - .6949).$$

Curve (5). Potential drop due to the inductance of the armature, equal to $L\frac{d^2q}{dt^2}$. same as curve (2), Fig. 8.

Curve (6). Potential drop between the apex and the earth, points A and E, Fig. 1. This may be obtained by adding curve (2) and curve (3).

$$\text{Curve } (6) = \text{curve } (2) + \text{curve } (3)$$

or, by subtracting (4) and (5) from (1),

$$\text{Curve } (6) = \text{curve } (1) - \text{curve } (4) - \text{curve } (5).$$

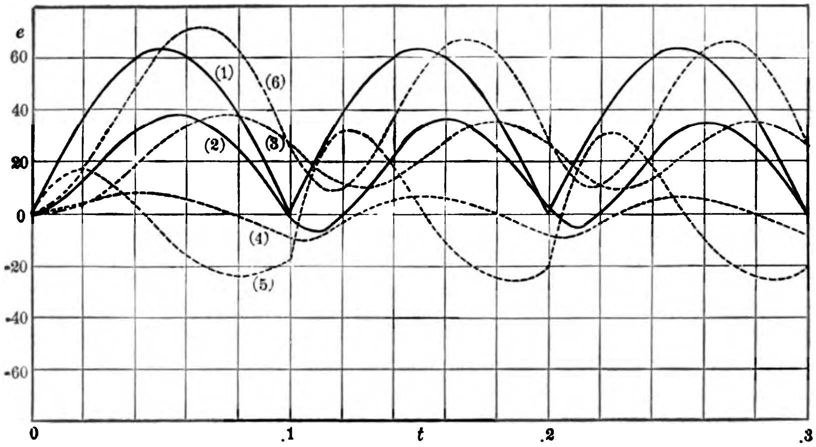

Fig. 11.

Curves of pulsating electromotive forces corresponding to those of Fig. 10. Equations of corresponding curves are the same for the first semi-cycle. For the second and succeeding semi-cycles the equations may be derived as those in Fig. 10.

THE TWO SPECIFIC HEATS OF GASES.

By W. P. Boynton.

MOST discussions and determinations of the ratio of the two specific heats of gases are based upon equations which apply strictly only to that abstraction known as the ideal gas. The external behavior of this ideal gas is given by the equation

$$pv = RT$$

where R is a constant, and T is the temperature on the absolute thermodynamical scale. Both the specific heats of the ideal gas, C_v, that at constant volume, C_p, that at constant pressure, are constant, and hence also their ratio, C_p / C_v. In actual gases both the specific heats and their ratio may and usually do vary.

The kinetic theory of gases suggests a series of values for the ratios of the specific heats, 1.667, 1.4, 1.333, 1.2857, etc., and some have affirmed that this theory could account for variations which would give values slightly less than these, but not for those slightly greater.

Some of the principal causes for variation, such as actual or approaching dissociation, will make the apparent specific heats greater, and since their difference is very nearly constant, their ratio becomes less. But some common gases give ratios slightly in excess; air and its main constituents, oxygen and nitrogen, give values averaging about 1.405, instead of 1.4.

In view of these variations I have tried to analyze the methods of measuring this ratio for a gas following van der Waals' equation,

$$(p + a / v^2)(v - b) = RT$$

which is valuable as a second approximation, coming somewhat nearer to the behavior of actual gases than does the equation for ideal gases. To restrict ourselves to the simplest form of mathematical discussion, we will not simply regard a, b and R, but also C_v, the specific heat at constant volume, as constants. Then the equation of the first law of thermodynamics can be shown to take the form

$$dQ = C_v dT + \left(p + \frac{a}{v^2}\right) dv.$$

In order to find the value of C_p it is necessary to eliminate dv. Multiplying out van der Waals' equation we have

$$pv - pb + \frac{a}{v} - \frac{ab}{v^2} = RT$$

and differentiating,

$$pdv + vdp - bdp - \frac{a}{v^2} dv + \frac{2ab}{v^3} dv = RdT$$

dropping the term $\frac{2ab}{v^3} dv$ as of a smaller order than the others, collecting, and solving for dv, we have

$$dv = \frac{RdT - (v - b)dp}{p - \frac{a}{v^2}}$$

$$\left(p + \frac{a}{v^2}\right) dv = \frac{p + \frac{a}{v^2}}{p - \frac{a}{v^2}} (RdT - (v - b)dp).$$

The value of the fractional coefficient is very nearly $1 + \frac{2a}{pv^2}$, and it immediately appears that in the new equation the coefficient of dT will be

$$C_v + R\left(1 + \frac{2a}{pv^2}\right).$$

Now since the other independent variable is the pressure, p, this is what must be defined as the true specific heat at constant pressure, C_p, and the ratio of the specific heats will be

$$\frac{C_p}{C_v} = 1 + \frac{R}{C_v}\left(1 + \frac{2a}{pv^2}\right)$$

which is slightly in *excess* of the value of an ideal gas, for which $a = 0$, namely,

$$\frac{C_p}{C_v} = 1 + \frac{R}{C_v}.$$

This result is practically the same as that obtained by Boltzmann.[1]

The most easily applicable method for the experimental determination of the ratio is that of the velocity of sound. The relation of this velocity to the other properties of the gas is given by the familiar equation

$$V = \sqrt{\frac{E}{D}}$$

in which D is the density of the gas, and E the elasticity, which in this case is the ratio of the increase of pressure to the relative diminution of volume, that is

$$E = -\frac{dp}{dv/v} = -v\frac{dp}{dv}.$$

Since the sound motions are very rapid, its compressions and expansions are to be regarded as adiabatic. Now the adiabatic condition for a gas following van der Waals' equation is readily found to be given by the equation

$$\left(p + \frac{a}{v^2}\right)(v - b)^{1+\frac{R}{C_v}} = K.$$

Solving for p and differentiating,

$$p = \frac{K}{(v-b)^{1+\frac{R}{C_v}}} - a/v^2,$$

$$\frac{dp}{dv} = -\frac{\left(1 + \frac{R}{C_v}\right)K}{(v-b)^{2+\frac{R}{C_v}}} + 2a/v^3$$

$$= -\frac{\left(1 + \frac{R}{C_v}\right)\left(p + \frac{a}{v^2}\right)}{v - b} + 2a/v^3$$

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[1] Gastheorie, II., p. 53.

$$E = -v\frac{dp}{dv} = \left(1+\frac{R}{C_v}\right)\left(p+\frac{a}{v^2}\right)\frac{v}{v-b}-\frac{2a}{v^2}$$

In an absolute determination I suppose that the actually determined velocity of sound is compared with that computed by the formula

$$V = \sqrt{\frac{p}{D}}$$

which is found for an ideal gas when the compressions are assumed to be *isothermal*. This would make the deduced "ratio of the two specific heats" equal to our value of E, above given, divided by p, that is,

$$\left(1+\frac{R}{C_v}\right)\left(1+\frac{a}{pv^2}\right)\frac{v}{v-b}-\frac{2a}{pv^2}$$

in which the second and third factors of the first term are each greater than unity, while the second term tends to offset this increase. Performing a part of the multiplication, omitting the terms of higher orders, and grouping, we have

$$1+\frac{R}{C_v}\left(1+\frac{a}{pv^2}+\frac{b}{v}\right)-\frac{a}{pv^2}+\frac{b}{v}.$$

Another method consists in letting the gas previously confined at a known pressure, expand suddenly to another known pressure, noting also either the resulting instantaneous temperature, or the final pressure when the original temperature has been restored. Lummer and Pringsheim,[1] employing the former of these two methods, use the formula

$$x = \frac{\log p_0/p_1}{\log p_0/p_1 - \log \theta_0/\theta_1}.$$

For a substance following van der Waals' equation the value of $1 + R/C_v$ would be the same expression with $p + \frac{a}{v^2}$ substituted for p, or the expression given above would be equal, changing θ to T, to

$$1+\frac{R}{C_v}\left\{1+\frac{\log\dfrac{1+\dfrac{a}{p_0v_0^2}}{1+\dfrac{a}{p_1v_1^2}}}{\log p_0/p_1 - \log T_0/T_1}\right\}$$

[1] Winklemann, Handbuch der Physik, II., 2, p. 380.

The evaluation of the corrective term is not simple unless one has experimental data to introduce, but on the assumption that the changes of volume and pressure are small an approximation may be made by the following device; for each logarithm of a ratio may be substituted the differential of the logarithm. The expressions resulting are somewhat complicated, but dropping terms of higher orders we obtain

$$1+\frac{R}{C_v}\left[1+\frac{a}{pv^2}\left(1-\frac{R}{C_v}\right)\right].$$

The three formulæ are most easily compared by taking concrete instances. Van der Waals'[1] gives values of a and b for various substances, computed by taking the atmosphere as the unit of pressure, and v as the ratio of the volume in a given state to that at 1 atmosphere and 0°C. In employing these values the three formulæ deduced thus reduce to the simple forms

$$(1) \qquad 1+\frac{R}{C_v}(1+2a),$$

$$(2) \qquad 1+\frac{R}{C_v}(1+a+b)-a+b,$$

$$(3) \qquad 1+\frac{R}{C_v}\left[1+a\left(1-\frac{R}{C_v}\right)\right].$$

The following table gives van der Waals' values of a and b for air, hydrogen and carbon dioxide, except that for hydrogen a is computed from b and the critical pressure, 15 atmospheres. The computed ratios are placed in the horizontal line with the number of the equation by which they are computed. The range of observed values is also noted.

It will be noticed that the effect of the correction term is in every case to increase the value of the ratio, except for CO_2 as computed by the second formula, where the preponderance of a makes the correction negative. These effects are of the same order of magnitude as the variations of the observed values of the ratios from the simpler values, 1.4 and 1.2857, but the experimental work is not

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[1] Winklemann, Handbuch der Physik, II., 2, p. 380.

	Air.	H	CO_2
a	.002812	.0000895	.00874
b	.00197	.00047	.0023
R/C_v	.4	.4	$2/7 = .2857$
1	1.40225	1.40007	1.2907
2	1.4011	1.40057	1.2826
3	1.40067	1.400021	1.2875
Obs.			
from	1.4015	1.385	1.265
to	1.4106	1.41	1.311

sufficiently concordant to show any systematic variation depending upon the choice of method employed.

It appears that the constant a is in general the measure of the variations to be expected, or in other words, we are to anticipate the greatest variation from the simple ratios in the case of those gases or vapors which depart most decidedly from the simple gas laws on account of the mutual attractions of the molecules. It is interesting to note that the correction factors are almost identical with those computed for the coefficients of expansion, and of change of pressure, which are

$$\alpha_p = \alpha\left(1 + \frac{a}{p_0 v^2}\right)$$

$$\alpha_v = \alpha\left(1 + \frac{a}{p v^2} + \frac{a}{p {v_0}^2} - \frac{b}{v_0}\right)$$

where the subscript $_0$ refers to the standard conditions at 0° C.

University of California,
Berkeley, Cal., April 15, 1901.

ON A FORM OF ARTIFICIAL SUBMARINE CABLE.

By Augustus Trowbridge.

IN teaching the principles of electricity and magnetism, I have often felt the want of some form of artificial submarine cable to illustrate the effect which capacity has on the propagation of electric disturbances along a conductor.

From conversations I have had with some of my fellow physicists, I have come to the conclusion that a description of a simple piece of apparatus designed to imitate the action of a submarine cable may be of interest to teachers of physics.

From the so-called telegraph equation we have that the time which must elapse from the closing of the "home end" of a circuit possessing capacity until the potential at the far end shall have risen to a certain fraction of its final value varies as the product of the resistance and capacity of the system. Stated another way: For different lengths of the same cable the time-lags in signaling vary as the squares of the length. Of course the actual values of the time-lags depend largely on the sensibility of the galvanometer used to detect the signals.

It is customary to look upon a cable as a long Leyden jar whose inner and outer coatings are respectively the conductor and the sea-water and in which the guttapercha sheathing is the dielectric. When one end of this system is put to the pole of a battery, the other pole of which is earthed, the first element of the conductor assumes the potential of the battery, while elements further from the home end still have their original potentials. The potential at any point on the cable rises, at first very rapidly and then more slowly, until after what is theoretically an infinitely long time has elapsed a stationary state is attained when the potential at any point depends only on the resistance of the circuit and the applied electromotive force.

It is during the variable period that the capacity of the system makes itself felt and that quantity together with the resistance is what determines the time-rate of variation of the potential at any point.

The time-rate of variation of the current strength at any point may be calculated if the variation of the potential is known. In non-mathematical language the way in which the current varies may be outlined thus: The uniform current strength in the conductor after the variable period is over and the steady state has set in is determined by the electromotive force of the battery and the resistance of the cable.

During the variable period the same quantity of electricity must be in motion as in the steady state but as a great portion of this is employed at first near the home end in charging the dielectric sheathing, the current in the first elements will be far above that which will exist uniformly in the whole conductor after the steady state has set in. For this reason, the current strength at the far end will have a value far below the final value. During successive time intervals the current will fall at the home end and rise at the far end where the galvanometer will be affected as soon as the current strength has reached a value at least equal to the figure of merit of the instrument.

In order that an artificial cable shall have an appreciable time-lag, both the resistance and capacity of the system must be great.

The necessary capacity of at least several hundred microfarads is rarely, if ever, to be found in the equipment of a department of physics on account both of its bulk and expense if it is of the ordinary tin-foil type.

In designing the apparatus described in this paper it was my aim therefore to make some inexpensive substitute for the ordinary form of capacity play the same rôle in the artificial cable that the gutta-percha sheathing does in the actual cable.

I naturally endeavored to make use of the great polarization capacity which a cell consisting of dilute sulphuric acid with platinum electrodes shows when the applied electromotive force has a value less than the maximum polarization of the cell.

The first to notice the great polarization capacity of electrolytic cells was, I believe, Mr. C. F. Varley who states in the Philosophical Transactions of the year 1872 that the capacity per square inch of platinum plates in dilute acid varies between 175 and 542 microfarads for charging electromotive forces varying between 0.02 and 1.6 volts.

In 1860 Mr. Varley constructed an artificial cable for the Atlantic Telegraph Company which wished one with which to demonstrate the feasibility of the submarine cable. I have been unable to find any description of this artificial cable but from references to it by Mr. Varley's contemporaries I infer that it was equivalent to a cable 1,200 miles long and that tin-foil capacities were used. Mr. Varley seems to have recommended the use of electrolytic condensers though as far as I can find he did not himself use them in the construction of a cable.[1]

The way in which the energy is stored up in the ordinary form of capacity and in an electrolytic capacity is, of course, very different but the effect of each in an electric circuit is the same and therefore in constructing a piece of apparatus to imitate the action of a submarine cable it is surely legitimate to use electrolytic capacity.

In a cable the capacity is distributed uniformly along the conductor while in an artificial cable we can only approximate this distribution by connecting the capacities as shown in the accompanying diagram.

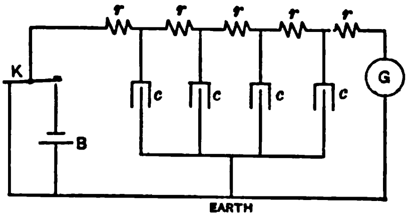

Fig. 1.

In the figure *B* represents a battery one pole of which is earthed, the other pole being connected to the double key *K*. This key serves to connect the conductor which is represented by the resistances *r*, first with the battery and then with the earth. The capacities which play the rôle of the dielectric sheathing are connected as shown. *G* is the galvanometer used to detect the arrival of a signal.

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[1] Since writing the above I have succeeded in finding a description of Varley's artificial cable in the "Notices of the Meetings of the Royal Institution," Vol. V., 1866–1869. The inference I drew from other sources as to the nature of the capacities used appears to be correct.

The electrolytic capacities which I used consisted of short lengths of glass tubing about 1 cm. in diameter with a platinum wire as an electrode sealed in to one end. The tube was filled nearly full of distilled water and the other electrode, which was a piece of platinum foil about 3 mm. wide, was corked in so as to dip about 5 mm. into the water.

In the cable which I have made I used 39 such cells arranged in 13 sets of 3 cells each. The 3 cells of each set were connected in parallel in the positions marked *c* in the diagram. The 13 resistances *rr* aggregated about one million ohms. The galvanometer had a figure of merit of 10^{-8} ampères which made a signal to consist of a small but very marked throw of the instrument.

It will be found convenient to mount the cells on a thin board in which a triple row of holes are drilled just large enough to allow the wire electrodes to project a few millimeters from the under side and to have this board rest on another in which are three troughs filled with mercury to serve as an earth connection for all the wire electrodes.

In this way if the board carrying the cells be lifted all the capacity is at once removed from the system and a signal is sent along the conductor with no appreciable time-lag. In other words, when the board is lifted the submarine cable becomes an overhead land line of the same length as the cable.

With the apparatus as here described the time-lag when the capacities are in, is very appreciable, being in the neighborhood of six seconds.

Of course the electromotive force of the battery used must be less than the maximum polarization of platinum electrodes in water and therefore a single Daniell or Leclanché cell is suitable.

PHYSICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.

FORCE DUE TO "CONTINUOUS IMPACT."

By Frederick Slate.

IN several well-known cases physical importance attaches to forces which are experienced as a result of some sustained process which consists of a series of impacts. It is desirable, therefore, that the idea underlying the measurement of such forces should be placed in the clearest possible connection with familiar principles of mechanics. The instances in question are usually made to depend upon the thought that force is the time-rate of momentum, the time-integral (impulse) of force being equal to the change of momentum in the line of the force. In symbols,

$$\int_{t_1}^{t} Pdt = m(v - v_1); \quad P = \frac{d}{dt}(mv). \qquad (1)$$

And for "steady" conditions (constant force),

$$P(t - t_1) = m(v - v_1); \quad P = \frac{m(v - v_1)}{t - t_1}. \qquad (2)$$

Equation (2) is then extended to the process of (steady) continuous impact, such as that of a water-jet against a fixed surface, by associating the time-factor with m. This gives $\frac{m}{t - t_1}$ as the mass per second reaching the surface, while $(v - v_1)$ is the velocity-change produced successively in each part of the impinging stream. The ordinary formula is derived thus,

$$P = qv = a\delta v^2. \qquad (3)$$

Here q denotes mass per second, δ density, a cross-section of jet; the impact being so arranged that the speed *in the line of the jet* is reduced to zero.

The "dimensions" of this result are right, and it is not proposed to deny the legitimateness of the argument upon which it rests, though the reasoning may be more formally correct than convincing. For equation (1) is generally derived in connection with the continued action of force upon the same mass. The application of the equation must be somehow justified, when the permanent factor is change of speed and not mass, and the other factor represents an aggregate of differential masses; not an aggregate of differential speed-changes. The purpose of the present note is to present a supplementary point of view, which confirms the results that are ordinarily accepted on the grounds quoted above. A simplified case will suffice to make the thought plain.

Let a series of equal masses m, of the same material in the form of spheres, be dropped from a given height, at equal intervals of t seconds, upon the horizontal surface of a plate of large mass. If v_1 and v are the vertical speeds just before and just after striking, the total change in momentum within each interval t is $m(v - v_1)$. The average acceleration for the interval is then $\frac{v-v_1}{t}$, and the average force (stress) is $m\frac{v-v_1}{t}$. If now each mass m be divided into n equal parts, which are dropped at equal intervals of $\frac{t}{n}$ seconds, the average stress is, as before,

$$\frac{m}{n} \cdot \frac{v-v_1}{\frac{t}{n}} = \frac{m(v-v_1)}{t}. \tag{4}$$

In other words, the time-average of the stress due to the impacts is not altered by the supposed distribution of the original mass among any number of bodies, other essential conditions remaining unchanged.

For $t = 1$, $n = 1$, and practical values of m, the curve showing stress as a function of time will consist of separate and equal sharp peaks, connected by portions of the time-axis itself which correspond to intervals of zero stress intervening between the periodic impacts. There will be violent fluctuations above and below the average value of the stress. As n is taken larger, the number of peaks for a given time increases, their height diminishes, and the departures from the average stress are reduced in magnitude. It is possible to assign a value to n which shall make the peaked curve lie as close as is desired to the straight line representing the average stress. The final substitution of the line for the curve amounts to the adoption of a "statistical average," in place of a quantity affected with rapid and small variations, such as gas-pressure due to molecular impacts. Or we may proceed to the (mathematical) limit for *continuous* impact. Then $dm = qdt$ vanishes with dt, the change in speed for dm is produced "instantaneously," and force (the product of mass and acceleration) appears in the indeterminate form $P = 0.\infty$. On writing the limit of equation (4) we find

$$P = \lim_{n=\infty} \left[\frac{m}{n} \cdot \frac{v - v_1}{\frac{t}{n}} \right] = q\,(v - v_1). \qquad (5)$$

This is a steady value; *i. e.*, a *sustained average.*

It is instructive to notice the relation between this conception of the process, and the degree of approximation to steady, continuous current which depends upon the construction of a dynamo-armature in segments.

University of California.

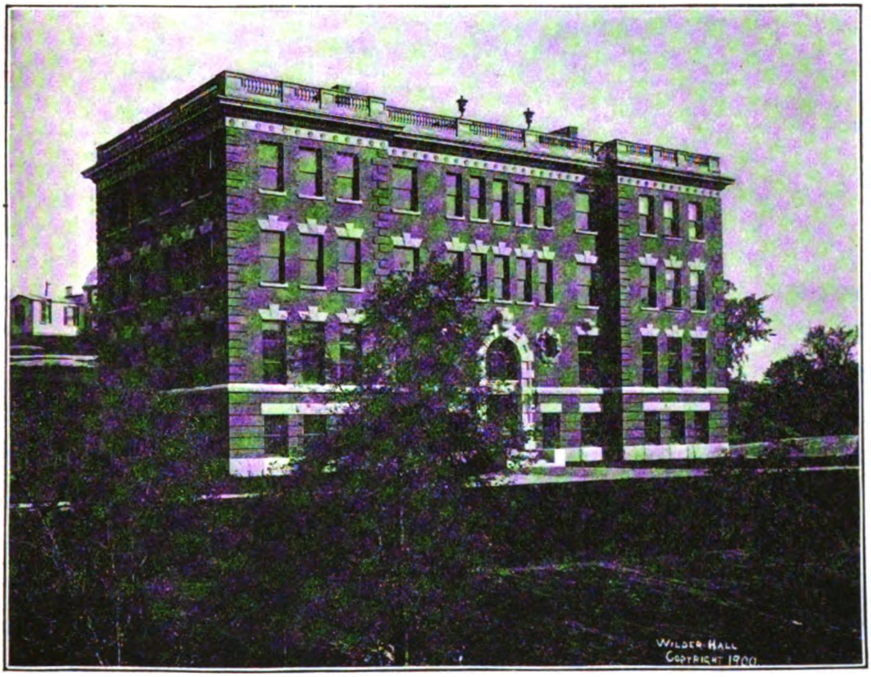
THE WILDER PHYSICAL LABORATORY OF DARTMOUTH COLLEGE.

By E. F. Nichols.

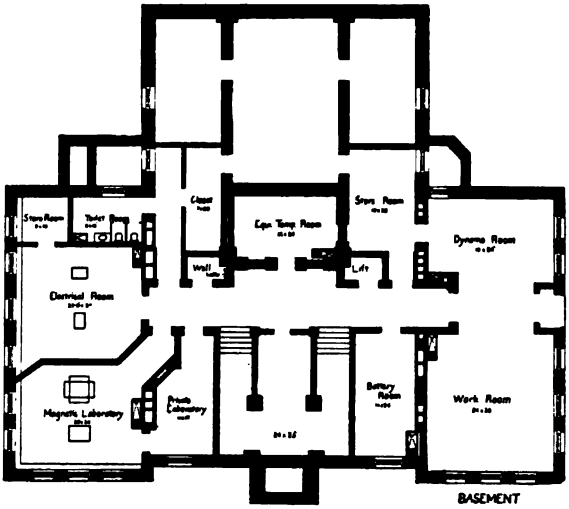
THE Wilder Physical Laboratory, the gift of the late Charles T Wilder, of Wellesley, Mass., was completed in September, 1899. The building, of which an exterior view and floor plans are reproduced here, is of brick with white granite trimmings. It has a frontage running east of north and west of south of 107 feet with a depth of 56 feet, and a rear projection 55 by 35 feet.

The basement section contains a workshop and dynamo room, equipped with two dynamo generators which, in common with the machine tools of the workshop, are supplied with power from a six-horse-power Pelton water wheel. The shop is provided with good metal- and wood-working lathes, and such other machine and hand tools as are necessary for the repairing and building of simple instruments. The storage battery room is stocked with 30 chloride cells (later to be increased to 60) of the type E, 5 class. These are connected in pairs to a mercury cup switchboard, permitting the grouping of the cells in a great variety of ways. This switchboard is connected to a main switchboard by three independent circuits, which makes possible a division of the battery into three sections for simultaneous use in different parts of the building. In the construction of the northwest corner of the building as high as the second floor, the use of iron has been avoided wherever possible, thus giving a practically iron-free magnetic laboratory in the basement. The basement further contains a large constant temperature room and an electrical laboratory.

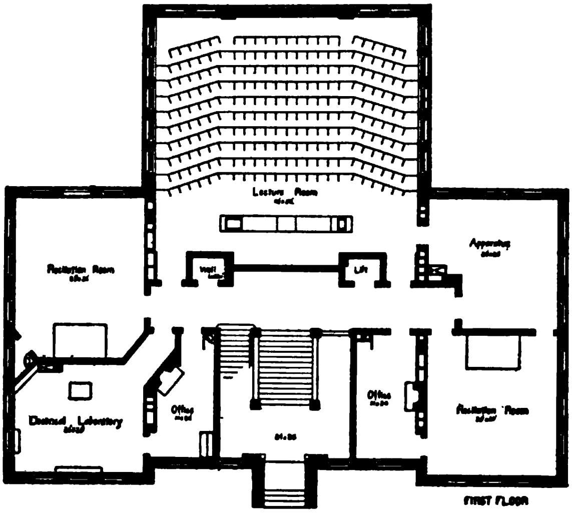
A lecture room on the first floor, seating 200, affords every convenience for the purposes of a lecture room for general physics. The windows can be darkened by shades operated by water power from the lantern table in the rear of the room. This table, not



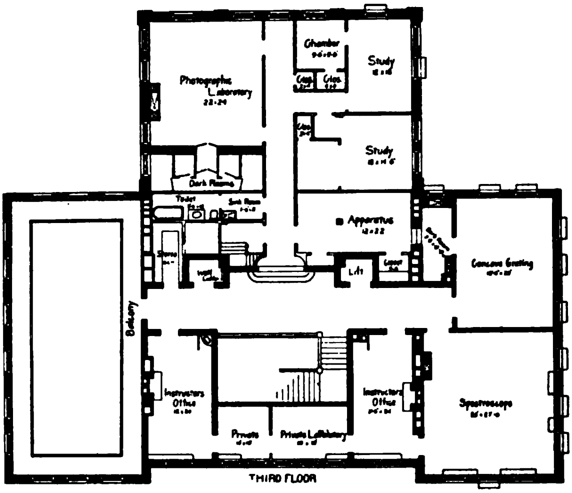
Wilder Physical Laboratory.

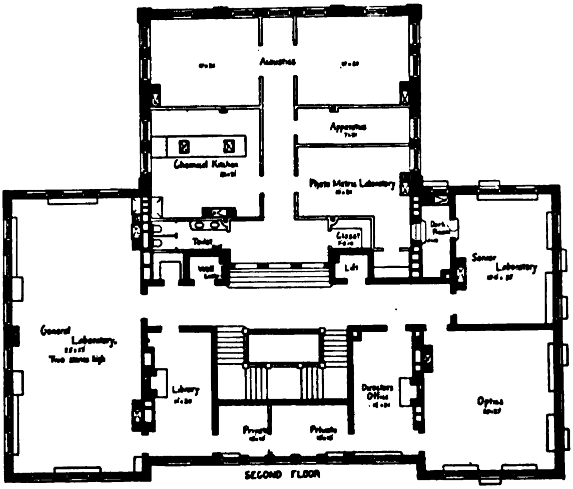


BASEMENT



FIRST FLOOR


Photographic Laboratory
22×24
Chamber
Study
Clos.
Clos.
Clos.
Study
Dark Rooms
Toilet
Sink Room
Apparatus
12×22
Stores
Lift
Closet
Concave Grating
Balcony
Instructors Office
Private
Private Laboratory
Instructors Office
Spectroscope
THIRD FLOOR


Acoustics
Apparatus
Chemical Kitchen
Photo Metric Laboratory
Toilet
Closet
Dark Room
Lift
Senior Laboratory
General Laboratory.
Two stories high
Library
Private
Private
Directors Office
Optics
SECOND FLOOR

shown in the plans, is provided with two power circuits to the main switchboard, with water connections and sink, illuminating gas, air under pressure, oxygen and hydrogen. The lecture table, 25 feet in length, is provided with all the conveniences of the lantern table, and steam in addition. In front of the white finished wall, used as a projection screen behind the lecture table, is a nest of movable blackboards. A roll screen is mounted on the north wall, and at an angle to it, in line with the lecture table, so that a projection lantern may be used in the front part of the room. The lecture and lantern tables, as well as all rooms in the building, are supplied with separate signal circuits, meeting in a telephone switchboard on the second floor. Thus clock, chronograph and other signals may be sent from or to any part of the building. The walls of the lecture room and those of the corridors and nearly all of the laboratory rooms are finished in dark red brick laid in tinted mortar. The room is lighted with incandescent lamps arranged between the open ceiling timbers. An apparatus and preparation room adjoins the lecture room. From a heliostat in a south window of the apparatus room a sunbeam can be projected along the lecture table.

The first floor contains, further, two recitation rooms, offices, and a research laboratory. This, like all of the other laboratory rooms, has slate shelves set in the walls at table height, has water connection, sink with slate draining boards and connections for illuminating gas and compressed air, and one or more independent power circuits to the main switchboard. The general lighting is from overhead fixtures, but for the lighting of scales or special work, wall sockets which may be plugged for portable lamps, are placed at convenient intervals.

The north end of the building, beginning with the second floor, is given up to the general laboratory. The room is open to the roof, giving great height and unusually good light. The wall space at the height of the third floor is made available for the mounting of wall apparatus by a balcony around the room.

The laboratories at the south end of the second and third floors are fitted with black shades for optical work. The southeast rooms on both floors have dark-rooms adjoining. In addition to the piping in other parts of the building, provision is here made for oxygen and hydrogen. These rooms have additional slate shelves outside the windows for heliostat and other purposes. The corridors and doors of connecting rooms are so arranged with reference to the south windows that a beam of sunlight can be sent into many of the rooms on the north side of the building.

The portion of the second floor above the lecture room contains a photometric laboratory, a chemical laboratory, an apparatus room and two other laboratories. The rear projection on the third floor contains an apparatus room, a photographic laboratory with four developing rooms, and two lodgings for the assistants in the department.

The roof of the building is flat, adapting it for meteorological or other observations. It is accessible by both a stairway and an elevator which runs from the basement to the roof level. A neighboring shaft like the elevator well, gives a free opening 61 feet deep, suited to experiments with falling bodies for the determination of air friction, to pendulum experiments and to the measurement of elasticity and fatigue in wires.

The building is supplied with steam from the college heating station. The heating is almost entirely indirect, providing adequate ventilation. All of the rooms have direct coils which may be used in extreme weather. The lighting is by alternating current. The wiring for lighting and power circuits is enclosed in iron conduits.

The building is after plans by Mr. C. A. Rich, of New York. Credit for the carefully planned interior arrangement and details is due to Prof. Charles F. Emerson, who was assisted in parts of the work by Prof. Edwin B. Frost, Dr. A. C. Crehore and the writer.

The equipment of the laboratory is being carried forward by the income from funds left for the purpose by Mr. Wilder.

ON A METHOD FOR THE DETERMINATION OF THE CRITICAL VELOCITY OF FLUIDS.

BY H. T. BARNES AND E. G. COKER.

IT has been shown by one of us[1] that if water be heated while flowing through tubes at velocities less than the critical velocity, in which the motion is in the form of parallel lines or "stream-lines," that the distribution of heat is not uniform. In the case where the heat is applied to the outside of the tube, as in the experiments of L. Graetz,[2] only a few layers of water in direct contact with the tube will be heated, the inflow water passing directly through the center unheated. In the case where the heat is received from a central wire, the hot water flows along the wire leaving the sides of the tube unheated. It is quite otherwise for flows beyond the critical velocity, in which case the flow is eddying and sinuous, and the distribution of heat, throughout the water-column, uniform. Since the passage from direct to sinuous motion takes place suddenly, the attainment of the critical velocity may be very sharply determined by measuring the sudden change in temperature in the water-column. We first undertook to observe this for a tube heated on the outside, by measuring the increase in resistance of a platinum wire threaded through the center of the tube. Our preliminary experiments by the method of color bands showed us that the presence of the wire, at least for a tube of ½ an inch diameter and a wire 6 mils in diameter, had apparently no influence on the critical velocity. Although this method proved to be quite satisfactory, we found that it could be more simply accomplished by placing the bulb of a sensitive mercury thermometer in the path of the moving column of water just as it emerged from the tube. This had the advantage of giving us the true temperature of the water, as well as showing us the attainment of the critical velocity.

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[1] Proc. Roy. Soc., 67, 238 (1900).

[2] Pogg. Ann., 18, 79 (1882).

It was a matter of considerable surprise to see the sudden jump of the thermometer thread, denoting the change in the character of the flow.

That the change in the thermometer reading indicates the point at which the steam-line motion breaks down can be shown for glass tubes by introducing the ordinary color-band test, in which case the band disappears at the same moment the jump on the thermometer take place. The appearance of flashes, occasioned by the momentary breaking down of the flow and its subsequent return to stream-line motion resulting from initial disturbances in the tank of water supplying the steady flow, are at once shown by an oscillation in the thread of the mercury thermometer, the reading going up and down with each flash. For a change in the reading of the thermometer, sufficient to observe, it is not necessary to have more than a few degrees difference in temperature between the water flowing through the tube and the walls of the tube, but in order to preserve perfectly uniform conditions, the walls of the tube must be kept at a constant temperature. This is accomplished by passing the tube through a water bath thoroughly stirred.

It would appear perhaps that there remains little to be accomplished in commencing an investigation into the question of the laws governing the flow of a liquid through a pipe—whether it should be direct or sinuous. Osborne Reynolds, Phil Trans. 1884, carried out an important investigation some years ago which treated the question both mathematically and experimentally, and gave us the laws governing the resistance of pipes for flows above and below the critical velocity. Briefly, the two methods of study adopted by him were the measurement of the point at which stream-line motion broke down, by the phenomenon of color bands, and the change from direct to sinuous motion as shown by the change in slope of the logarithmic homologues of velocity and pressure. In the first case the water entered the tube in a state free from agitation, and the breaking up of the stream-lines representing the breaking down of an unstable flow. In the second case the water entered the tube in a state of disturbance, which became direct in its passage through the tube, the arrival of the critical velocity being shown by the state of disturbance not disappearing from the flow.

A large difference was found between the values of the critical velocity measured by the two methods, which corresponds to the velocity at which stream-line motion breaks down and eddy motion changes to direct.

Owing to the advantages offered by the direct thermometric method of studying the critical velocity over the more complicated method of color bands, observations may be made on tubes other than glass. The experimental arrangements may also be made much less complicated and more suitable for fulfilling required conditions. We have already carried out some experiments to test the method on a small scale, and our preliminary results have so far shown for the sizes of tubes tried, that the critical velocity varies inversely as the diameter, according to Reynolds' well-known formula

$$v = \frac{1}{B} \cdot \frac{P}{D}$$

where B is a constant
D is the diameter
and $P = (f)\ T.$
T being the temperature centigrade.

It seems desirable to study more in detail the validity of this simple law for tubes of a greater diversity of size than Reynolds used, and more particularly for tubes of great diameter. Our experiments have not as yet been sufficiently precise to enable us to fix on the extent of the application of this formula, but as far as we have gone it is at all events approximately true. Reynolds' observations were made for only three tubes varying from 2.6 cm. diameter to .79 cm., while the effect of pressure and temperature on the critical velocity is by no means as satisfactorily known as seems desired.

Through the kind interest of Prof. H. T. Bovey, Dean of the Faculty of Applied Science, the facilities of the McGill hydraulic laboratory have been placed at our disposal, where more refined apparatus than was possible in our preliminary trials is rapidly being constructed, and where special facilities are offered for carrying out the experiments on a large scale.

McGill University, April 27, 1901.

NOTE ON SOME MODIFICATIONS OF ELECTRIC DISCHARGES CAUSED BY DIELECTRICS.

BY K. VON WESENDONK.

IN view of the paper recently published by Mr. Humphreys[1] in the PHYSICAL REVIEW, I may perhaps be permitted to draw attention to some experiments briefly described by me[2] in Wiedemann's Annalen. It is said in my paper that the effect upon an electric discharge of bodies brought near showed some peculiar differences of which, though they were surely already known, not much notice seemed to have been taken until then; and that therefore a brief description of the phenomena might not be quite useless.

In the first place, the effect of a metal plate held near the pointed pole of a spark gap, plate and pole being at the same potential, is considered. All other circumstances remaining unaltered, this effect consists chiefly in an elevation of the potential belonging to the pointed pole provided this pole be insulated. In case it has been connected to the earth so that the discharge only takes place by the influence of the other, necessarily isolated, pole, the latter will show an increase of potential. The plate brought near to the pole by changing, as may be seen, the shape of the equipotential surfaces in the vicinity of the point, reduces the potential gradient there and renders, thereby, the outflow of electricity more difficult. Thus the nature as well as the shape of the luminous discharge may be altered; for instance, instead of the electric brushes or glow discharges which alone were formerly present, one may now also observe, more or less frequently, the occurrence of sparks. As is pointed out in my paper, these experiments seem on the whole to be in favor of the Melsen's system of lightning conductors.

With dielectrics some other phenomena were observed. When a glass tube was held near to the positive pole of a spark gap, both terminals of which consisted of balls, then in certain positions and at suitable distances of the electrodes from each other, sparks much longer than those observed under ordinary circumstances appeared both when the positive pole was insulated and when it had been connected to the earth and the discharge went on under the influence of the insulated kathode. In neither case could any sensible change of potential at the insulated pole be discovered. The dielectric when brought near to the anode generally causes beautiful brush discharges which will then be more or less frequently transformed into sparks; but it is also possible to produce such sparks by means of the dielectric without the preceding brush discharge being seen. Quite similar is the effect of an insulated conductor brought near to the anode. In this case also the length of the sparks is considerably increased without any sensible elevation of potential. Held near to a point the dielectric, or an isolated metal piece, gave sparks but a little longer than usual, accompanied by a slight elevation of potential. Held between the poles both were efficacious only when the electrodes were very near each other. A series of small insulated pieces of metal interposed between the electrodes did not show sensibly more influence than that due to the one nearest the anode alone. In the same way water spray blown between the poles had no sensible effect.

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[1] Humphreys, PHYSICAL REVIEW, Vol. XI., page 79, 1900.

[2] Wesendonk, Wiedemann's Annalen, Vol. 49, page 296, 1893.

It will be seen that the curious phenomena with which the paper of Mr. Humphreys deals have not entirely escaped former observation and that something has already been published concerning them. The explanation I believe to be the following: Since the dielectric, or the insulated piece of metal, and the nearer electrode are not at the same potential, a discharge may easily take place between the two. Now the positive discharge, as I believe to have shown, is very apt to bring down the resistance of the medium between the poles, at least partially, and so to allow a spark or a large brush discharge to take place where such cannot appear under the usual circumstances. A positively charged body is known to be very fit to give long sparks and these, I believe, are only obtained in consequence of the brush discharge which precede them.

BERLIN, Jan. 30, 1901.

A SIMPLE APPARATUS FOR ILLUSTRATING FORCED VIBRATIONS.

By John R. Benton.

THE principle of forced vibrations can be illustrated by an apparatus consisting merely of a rubber band, a piece of string, and a weight.

In the adjoining figure *AB* represents the rubber band, hung from *A*; to its lower end is fastened a (non-extensible) string *BC*, on which the weight *W* is hung. If the weight is displaced vertically, and then let go, it will execute a harmonic motion, due to the elasticity of the rubber band. The period of this harmonic motion will be independent of the length of the string *BC*. If the weight is displaced horizontally, and then let go, it will swing like a pendulum. The period of this motion will be $2\pi\sqrt{\frac{AC}{g}}$ and can therefore be changed by changing the length of the string *BC*.

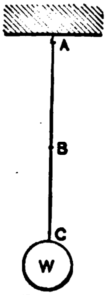

Fig. 1.

The centrifugal force of a pendulum varies periodically from 0 at the end of a swing to a maximum at the middle of a swing. If the amplitude is small, so that we may put $\theta = \sin\theta$, the centrifugal force *F* at any time *t* after passing the middle is given by the expression

$$F = mga^2 \cos^2 \sqrt{\frac{g}{l}}\, t$$

where *m* is the mass of the pendulum bob, *a* the amplitude, and *l* the length of the pendulum.[1]

---

[1] The rigorous expression for *F* is $F = 4mg \sin^2 \frac{a}{2} \operatorname{cn} \sqrt{\frac{g}{l}}\, t$, where $\operatorname{cn} \sqrt{\frac{g}{l}}\, t$ is the cosine of the amplitude of $\sqrt{\frac{g}{l}}\, t$ in the elliptic integral $\sqrt{\frac{g}{l}}\, t = \int_0^{\phi} \frac{d\phi}{\sqrt{1 - \sin^2 \frac{a}{2} \sin^2 \phi}}$.

The principle of the apparatus here described depends on the action of the variation of F in producing vibrations in the direction of the suspending string. The period of a complete cycle of variation of F is equal to half the period of the pendulum. If the weight be adjusted at such a position on the string BC that the period of the pendulum motion is twice that of the elastic vibration, and if a pendulum motion be given to the weight, then violent vibrations in the direction of the suspension will soon be set up. If however the weight is so adjusted that the period of the pendulum is equal to that of the elastic vibrations, or equal to ¼ of their period, then the pendulum swings almost as steadily as when its suspension is non-extensible.

I found it convenient to use a rubber band of cross section about 4 mm.^{2} (when not extended), and a weight of about 600 gr. The length of the pendulum when the forced vibrations attained their maximum amplitude was 40 cm.

Princeton University.

NEW BOOKS.

Lectures on the Lunar Theory. By JOHN COUCH ADAMS. Edited by R. A. SAMPSON. Pp. 88. Cambridge, 1900.

This set of eighteen lectures on the theory of the moon's motion is taken, without change of any sort, from the complete collection of Adams' scientific papers. The two volumes, containing these papers, were printed at Cambridge in 1896 and 1900. The first volume contained all of the published articles; the second was made up from the manuscript material left by Professor Adams, and the lectures are there published, for the first time. For those who have not means of access to the full collection, the present reprint will be of value.

The lectures do not cover all of Adams' investigations upon the subject. They have been made up from the notes found among his papers, prepared for current use in his lectures, and changed from year to year, developing with that constant care and interest which he gave to this problem for many years.

The first lecture has been built up from the notes taken by those who had the fine opportunity of listening to the delivery, and is historical in treatment. Sufficient material was found among the manuscript papers, to supply the remaining lectures in full. Although not arranged nor completed by Adams, for any such purpose, his finished and precise method of carrying on his current work made the process of selection and combination direct and certain.

After developing the general equations for the moon's motion, the treatment followed is by separating the special problems. The Variation is first taken up, the inequality that Newton first solved. The Parallactic Inequality, the Annual Equation and the Evection are successively treated, with the resulting determination of the numerical constants. These accord well with those determined by Delauney, in his treatise upon the Theory of the Moon. The change of the Eccentricity and the motion of the Node have special treatment.

This course of lectures, it appears, did not include the evaluation of the amount of the Secular Acceleration of the moon's mean motion; though Adams had completed his investigation, and published his result in 1853, several years before the commencement of these lectures. The controversy following the publication of this constant is historical. His own contribution to the discussion, printed in 1860, is a model of earnest, vigorous and at the same time courteous statement.

Nor are any of the results from his investigation of the Lunar Parallax given here. Aside from these lectures, fully a quarter of Adams' published articles were upon subjects connected with the Lunar Theory.

The lectures close with a discussion of Hills' method of treating portions of the same problem. In some respects the two great mathematicians had been working on parallel lines. While the details of the processes employed differ, the methods and results confirm each the other.

R. H. Tucker.

Atmospheric Radiation. By Frank W. Very. United States Weaher Bureau. (Bulletin G of the Department of Agriculture.) Washington, 1900. Pp. 134.

In this important memoir Professor Very presents the results of an extended investigation of the very difficult subject of radiation from the various components of the atmosphere. The work includes, from the nature of the case, the study, separately, of radiation at various temperatures and pressures, from dry air, aqueous vapor and carbon dioxide.

The problem of atmospheric radiation is greatly complicated by the fact that both moisture and carbon dioxide possess great absorbing power for the particular wave-lengths which they àre capable of radiating so that they become opaque to their own radiation even in layers of moderate thickness. The opacity of gases is shown to depend upon the selective character of their radiation, so that those gases which are powerful radiants of certain wave-lengths, in thin layers become more rapidly opaque to their own radiation than poorer radiators, such as dry air. In the case of the two constituents just mentioned, namely, water and carbon dioxide, it was found for example that the radiation with increasing depth of layer rapidly approaches a maximum so that a five-foot layer of the latter gas radiates little more than a two-foot layer and no more than a three-foot layèr; while dry air radiates very nearly in proportion to the depth. The extraordinary fact previously noted by Paschen that vapors such as ammonia, carbon dioxide, etc., have in the regions of maximum radiating power approximately equal to that of a black body, is abundantly confirmed. Various important applications of the results of this research to the complex problems of meteorology are treated in the closing pages of the memoir.

To the physicist Professor Very's work is of very great direct interest, not only for the results which he has obtained but as an admirable and inspiring example of the thorough-going, exhaustive and successful experimental research upon an intricate problem.

E. L. N.

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